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16. ABSTRACT
Large quantities of volatile organic substances are emitted from mobile and stationary sources in the United States. When the US, east of 105° west longitude is divided into 80 by 80 km grids, most of these grid areas east of the Mississippi River and many west of the river, have organic emissions of at least 10,000 to 20,000 tons y^{-1} from area sources. In addition, point sources outside of large cities involving emissions from petroleum industrial processes and chemical manufacturing contribute substantially. Sources of natural emissions are distributed much differently than the sources of anthropogenic emissions. The emission rates are much higher throughout the year in the southern United States. Essentially all of the available measurements for biogenic hydrocarbons are related to isoprene and monoterpenes, particularly from forest species. There is no current evidence that the volatile natural organic compounds as emitted have adverse health or welfare effects. The interest and potential concern has been focused on formation of secondary atmospheric products from the natural organic compounds. All the pertinent results on product formation needs to be considered adequately. The capability of these natural organics to contribute to formation of ozone, aerosols and other products must be carefully assessed.

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REVIEW: NATURAL VOLATILE ORGANIC SUBSTANCES AND THEIR EFFECT ON AIR QUALITY IN THE UNITED STATES

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Abstract—The literature on sources, emission rates, emission inventories, ambient air concentrations, lifetimes and reaction products of natural volatile organic compounds has been reviewed. Relationships between emission inventories and air quality measurements are considered. The effectiveness of natural hydrocarbons in contributing to ozone formation and aerosol formation in ambient air are discussed. It is concluded that natural hydrocarbons do not contribute substantially to the formation of either ozone or aerosols in ambient air.

1. INTRODUCTION

Large quantities of volatile organic substances are emitted from mobile and stationary sources in the United States (U.S. Environmental Protection Agency, 1974; Radian Corporation, 1978). About 70% of these organic anthropogenic emissions are emitted from area sources (Clark, 1980). In addition, point sources outside of large cities involving emissions from evaporation from petroleum storage, petroleum industrial processes and chemical manufacturing contribute substantially, particularly in Texas, Louisiana and Oklahoma (Clark, 1980).

As will be discussed in detail later, the sources of natural emissions are distributed much differently than the sources of anthropogenic emissions. Isoprene and terpene emissions in rural areas usually are highest in the early summer and vary rapidly with season of the year. The emission rates are much higher throughout the year in the southern United States. In addition, isoprene and monoterpene emissions are known to have unique diurnal patterns. Superimposed on these wide variations, are other shorter period excursions in emissions reported in the literature. Essentially all of the available measurements for biogenic hydrocarbons (HCs) are related to isoprene and monoterpenes, particularly from forest species.

There is no current evidence that the volatile natural organic compounds as emitted have adverse health or welfare effects. The interest and potential concern has been focused on formation of secondary atmospheric products from the natural organic compounds. The earliest relationship claimed was between aerosol products of the terpenes and haze formation. Subsequently, more attention has been given to the potential of isoprene and terpenes to participate in O_3 formation in rural areas and to contribute to the O_3 inflow to urban areas downwind.

To understand the potential for contribution by natural volatile organics, the literature on emission sources, emission rates, chemical composition and variations with latitude, longitude, season of the year and time of the day must be reviewed. The ambient air concentration levels measured and the life-times of the natural organics must be considered. Finally, the capability of these natural organics to contribute to formation of O_3, aerosols and other products must be carefully assessed.

2. SOURCES OF NATURAL VOLATILE ORGANIC SUBSTANCES

A considerable number of volatile organic substances have been associated with emissions from natural sources. Most of the specific substances identified have been HCs. The measurement procedures available have been most useful for identification of HCs. The substances identified have included methane, ethane, propane, as well as higher molecular weight paraffinic HCs. The olefinic HCs identified include ethylene, isoprene and a number of monoterpenes. Several natural oxygenated organic substances also have been identified.

Methane is produced in very large quantities from natural sources (Altshuller, 1958). Bacterial fermentation processes in swamps, marshes, ponds, and lakes are the major biological sources. In addition, methane is lost in appreciable amounts through seepage of natural gas components through the soil to the atmosphere. Methane is also formed in coal deposits and lost to the atmosphere. Forest fires also contribute some methane to the atmosphere. One estimate of worldwide emissions of methane is 3×10^8 t y^{-1} (Koyama, 1963).

Ethane, propane, butanes, pentanes and higher molecular weight paraffinic hydrocarbons are emitted to the atmosphere along with methane in seepage of

Table 1. Composition of volatile organic compounds from vegetation[a,b]

Type	Location[b]	Time period	Total NMVOC $\mu g\ g^{-1}\ h^{-1}$	Isoprene	Myrcene	α-Pinene	β-Pinene	D-Limonene	Δ^3-Carene	Other olefins	C_2–C_6[c] alkanes	other C_6–C_{12} VOC
Wax myrtle	FL	day	7.5	0	0	9	4	trace	1	70	10	6
Red bay	FL	day	2.0	0	0	15	10	0	0	34	23	18
Sweet acacia	FL	day	5.9	0	2	64	7	4	0	3	10	10
Oranges	FL	day	9.3	0	0	0	0	2	0	57	20	21
Grapefruit	FL	day	4.3	0	0	11	0	0	trace	3	49	37
Tomatoes	FL	day	48.1	0	trace	0	0	32	8	25	16	19
Black mangrove	FL	day	1.3	0	0	0	0	0	0	0	32	68
White mangrove	FL	day	1.2	0	0	0	0	0	0	0	59	41
Red mangrove	FL	day	1.0	0	0	0	0	0	0	0	60	40
Elderberry	FL	day	4.8	0	0	0	0	0	0	0	58	42
Dahoon holly	FL	day	2.8	0	0	0	0	0	0	0	54	46
Red mulberry	FL	day	8.2	0	0	0	0	0	0	14	60	26
Oleander	FL	day	20	0	0	0	0	0	0	0	36	64
Viburnum	FL	day	2.6	0	0	0	0	0	0	8	50	42
Carolina ash	FL	day	0.5	0	0	0	0	0	0	0	32	68
American elm	FL	day	3.9	0	0	0	0	0	0	0	50	50
Okra	FL	day	9.8	0	0	0	0	0	0	0	57	43
California Western Sagebrush	CA[e]	day or night	—[e]	0	2	8	4	3	0	8[f]	N.A.	87[f]

[a] Measurements by bag enclosure technique samples. [b] Florida results from Zimmerman (1979a) with computation of percentage composition from flux measurements. [c] Predominately ethane and propane. [d] From Flyckt (1979). [e] From Westberg (1981) emission rate 13.3 $\mu g\ dm^{-1}\ d^{-1}$. [f] Includes camphene, camphor, 1, 8-cineole, cymene, β-phellandrene and γ-terpinene.

natural gas and from bacterial fermentation processes (Altshuller, 1958; Mayrsohn and Crabtree, 1976; Seila, 1981). Paraffinic HCs also were measured in bag enclosure samples collected from tree branches, field crops, grasses, mud flats and marshes in the Tampa Bay area of Florida (Zimmerman, 1979a).

Ethlene is emitted by fruits, flowers, leaves, roots and tubers. However, ambient air ethylene concentrations at rural sites usually are very small (Arnts and Meeks, 1981; Lonneman *et al.*, 1978; Seila, 1981). An average annual emission rate for ethylene from vegetation of 0.5 nl g^{-1} fresh weight h^{-1} has been estimated from which total annual emissions over the United States of ethylene of 1.8×10^4 t y^{-1} can be computed (Abeles *et al.*, 1971). This estimate also involves the assumption that on the average the U.S. is covered by one ton of vegetation per acre. This is a small emission rate compared to anthropogenic emissions of organics of 3×10^7 t y^{-1}.

The olefinic HC, isoprene, often is present in the ambient air in rural forested areas. Isoprene is the predominant HC emitted by a number of forest species including oaks, poplars, sycamores, willows, cottonwood, eucalyptus and palmettos (Rasmussen, 1972; Westberg, 1981; Zimmerman, 1979a). In addition, isoprene has been measured as an emission product along with monoterpenes from other forest species and cultivated plants (Table 1) (Zimmerman, 1979b).

The monoterpenes, especially α-pinene, β-pinene, D-limonene and Δ^3-carene have been measured by the bag enclosure technique as emitted from a variety of forest species and grasses (Tables 1, 2). Myrcene, β-phellandrene and terpinolene are reported from a few species (Zimmerman, 1979a, b).

Additional volatile organic substances were reported at substantial concentrations by Zimmerman in the Tampa Bay area (Zimmerman, 1979a). These substances were not identified but had gas chromatographic retention times in the range of C_6–C_{12} HCs (Tables 1, 2). Methyl chavicol, an ether, was identified and measured as a component of the emissions from Ponderosa pine in the Pullman, Washington area (Flyckt, 1979; Westberg, 1981). In the emissions from sagebrush two oxygenated organic substances, camphor and 1,8-cineole have been identified as major products (Flyckt, 1979; Tyson *et al.*, 1974).

Table 2. Composition of volatile organic compounds from grasses and some crops in Florida*

Type	24 h average emission rate, $\mu g\ m^{-2}\ h^{-1}$	Isoprene	Mycrene	α-Pinene	β-Pinene	D-Limonene	Δ^3-Carene	Other olefins	C_2–C_6† alkanes	Other C_6–C_{12} VOC
Mixed grasses	190	0	0	30	5	trace	1	1	40	23
Bahia	54	0	0	0	0	0	0	0	46	54
Bermuda	163	0	0	2	0	0	6	4	42	46
Clover	153	0	0	0	0	0	0	8	64	38
Penscola	144	0	0	7	2	0	0	0	55	36
Sawgrass	392	0	0	62	10	0	0	3	18	7
Strawberries	419	0	0	0	0	0	0	0	86	14
Beans	1565 day	75	0	0	0	0	0	0	19	6
	264 night	0	0	0	0	0	0	0	78	22

*From Zimmerman 1979(a) with computation of percentage composition from flux measurements.
†Predominately ethane and propane.

3. ENVIRONMENTAL EFFECTS ON EMISSION RATES OF BIOGENIC VOLATILE ORGANIC SUBSTANCES

Available research on environmental effects has been concerned with isoprene and monoterpene emissions from several forest species. Little is known about the effects of temperature, light intensity and other environmental effects on isoprene and monoterpenes from other sources or other volatile organic substances from biogenic sources.

The effects of temperature and light intensity on isoprene emissions and monoterpene emissions have

been investigated by Tingey and coworkers using plants in a gas-exchange chamber (Tingey, 1981; Tingey *et al.*, 1979, 1980). Emission rates were measured at five light intensity levels 0, 100, 200, 400 and 800 μE m^{-2} s^{-1} and in the temperature range from 20 to 46°C.

The emission rates of isoprene from live oak saplings were observed to increase with increasing leaf temperature at each light intensity (Tingey *et al.*, 1979). The functional relationship of emission rate with temperature was complex and different at each light intensity level.

The emission rates for the monoterpenes α-pinene, β-pinene, myrcene, D-limonene and β-phellandrene, from slash pine saplings were log-linearly related to temperature (Fig. 1) (Tingey *et al.*, 1980). The slope parameters for these monoterpenes were approximately equal, so the composition was nearly constant over the temperature range used. This result is consistent with the monoterpene vapor pressures being log–linear with temperature. At 35°C the percentage composition from slash pine computed from emission rates in μg C g^{-1} dry needle wt h^{-1} (Tingey *et al.*, 1979) was as follows: α-pinene, 52; β-pinene, 40; myrcene, 4; limonene, 2 and β-phellandrene, 2.

The emission rates for isoprene are sensitive to light intensity. The emissions of isoprene from live oak saplings increased with increasing light intensity at temperatures up to 40–44°C (Tingey *et al.*, 1979). In the dark, isoprene emissions were very low throughout the temperature range used. Similar behavior has been observed for other isoprene-emitting species (Rasmussen and Jones, 1973); Sanadze and Kalandadze, 1966). Unlike isoprene emissions, the emissions of monoterpenes were found to be constant at all light intensity levels at each temperature (Tingey *et al.*, 1980).

Measurements using the bag enclosure technique of emissions from several branches of red oak and ponderosa pine trees were made by Flyckt each month from May 1978 to June 1979 in Pullman, Washington (Flyckt, 1979; Westberg, 1981) [Figs 2(a) and (b)]. Samples were analyzed by gas chromatography and by a gas chromatographic/mass spectrometric system.

The seven monoterpenes, α-pinene, β-pinene, myrcene, Δ^3-carene, β-phellandrene, D-limonene and terpinolene along with the aromatic ether, methyl chavicol, accounted for most of the mass of volatile organic substances emitted from ponderosa pine (Flyckt, 1979). In addition, C_2–C_6 HC components constituted a small portion of the total emissions.

The monthly emission rates of these substances peaked in the spring, decreased rapidly through the summer and fall months, and started to increase again late in the winter (Flyckt, 1979; Westberg, 1981). The emission rate μg compound g^{-1} leaf biomass dry weight h^{-1} of Δ^3-carene in the May 1978 sample was

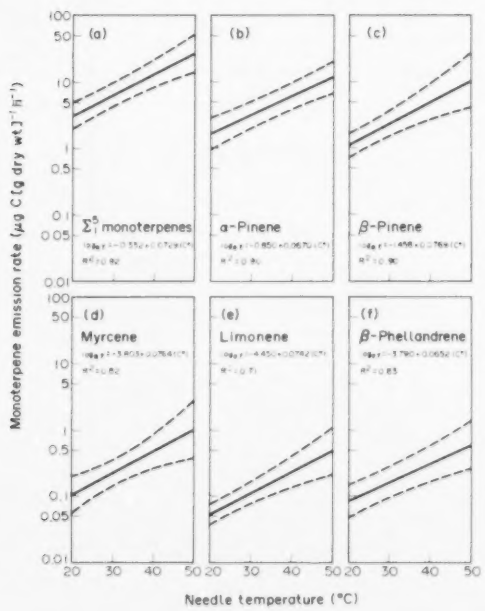


Fig. 1. The influence of increased temperature on monoterpene emission rates in slash pine. The dash lines are the 95% confidence bounds for the regression lines. (From Tingey *et al.*, 1980; Tingey, 1981).

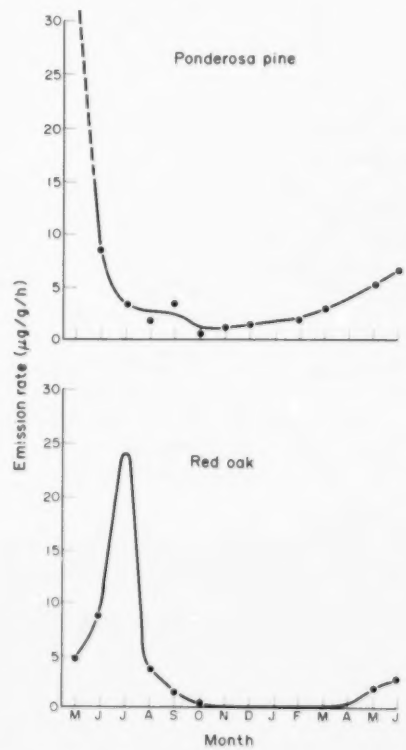


Fig. 2. (a) Emission rates of monoterpenes from ponderosa pine. (b) Emission rates of isoprene from red oak (from Flyckt, 1979; Westberg, 1981).

about equal to the sum of the emissions of all of the volatile organic substances in the other monthly samples. However, this particular value could be questionable. It was not reproduced the following year. The composition varied seasonally along with the emission rate. The monoterpene, Δ^3-carene, was the most abundant substance during much of the year (Flyckt, 1979). However, β-pinene made about an equal contribution during the summer months and exceeded Δ^3-carene during the fall months. The high concentration levels of Δ^3-carene originated from the oleoresin of the ponderosa pine. By summer, the β-pinene, the major component in ponderosa pine needle oil, was volatilizing at a substantial rate.

Isoprene accounted for from 60 to 80 percent of the total emissions from red oak during periods of significant isoprene emission (Fig. 2b). The remaining emissions consisted of numerous compounds at very low concentrations with retention times about the same as those of the monoterpenes (Flyckt, 1979). The monthly emission rate for volatile organic substances from the red oak increased rapidly during the spring, peaked in July, and dropped off rapidly to zero by November and began to increase again in the spring. The emission rate in July about equalled the sum of emission rates for all of the other monthly samples collected. For those seasonal conditions during which the isoprene emissions decreased to zero, the remaining emissions consisted of traces of numerous C_2–C_{12} volatile organic compounds.

In the same study (Flyckt, 1979; Westberg, 1981), a log–linear relationship was observed between the ratio of isoprene emitted by red oak to CO_2 absorbed with variation in temperature. A good correlation was reported between the isoprene emission rate and temperature.

The discussion above is concerned with emission rates from forest species (Tingey, 1981) also lists emission rates from soybean of 0.007 μg C dm^{-2} h^{-1} and from bushberries of 0.010 μg C dm^{-2} h^{-1}.

4. BIOGENIC EMISSION INVENTORIES

4.1. *Bag enclosure technique*

Several biogenic emission inventories have been developed for isoprene and the monoterpenes. In all of these studies samples were collected into Teflon bags enclosing the vegetation. Subsequently, the samples were transferred to electropolished stainless steel canisters for storage and subsequent analysis.

Samples were analyzed by flame ionization detector–gas chromatography using four columns to separate C_2–C_{12} components. An emission inventory for the contiguous United States has been developed using this method (Zimmerman, 1979b). Estimates of isoprene and monoterpene emissions were computed for each of the year in each of four geographical zones. The monthly average isoprene emissions by zone are plotted in Fig. 3 and the monthly average sum of isoprene plus monoterpene emissions are plotted in Fig. 4. The zones were selected by use of climatological temperature records. The zones were as follows: zone I, 45–50 N latitude; zone II, 40–45 N latitude; zone III, 35–40 N latitude; zone IV, 25–35 N latitude (Fig. 5). The computed results are dependent on the representativeness of the limited group of measurements of biogenic emissions and biomass (Zimmerman, 1979b).

These biogenic emissions show very large seasonal

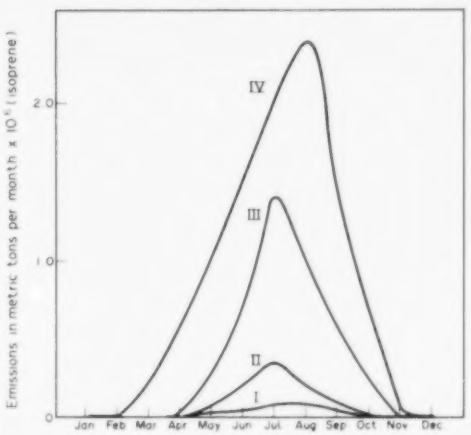


Fig. 3. Emission rates of isoprene by month of the year within four geographical zones in the contiguous United States (plotted from tabulated results in Zimmerman, 1979b).

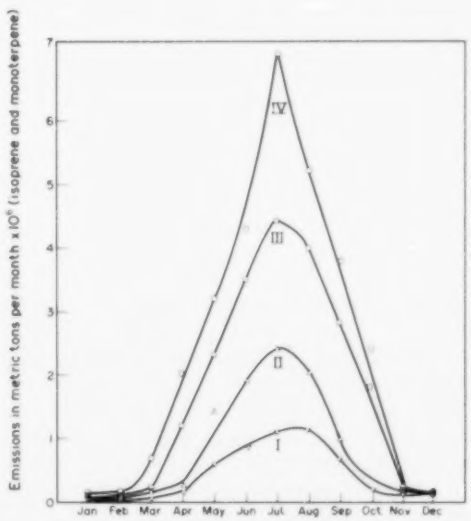


Fig. 4. Emission rates of isoprene plus monoterpenes by month of the year within four geographic zones in the contiguous United States (plotted from tabulated results in Zimmerman, 1979b).

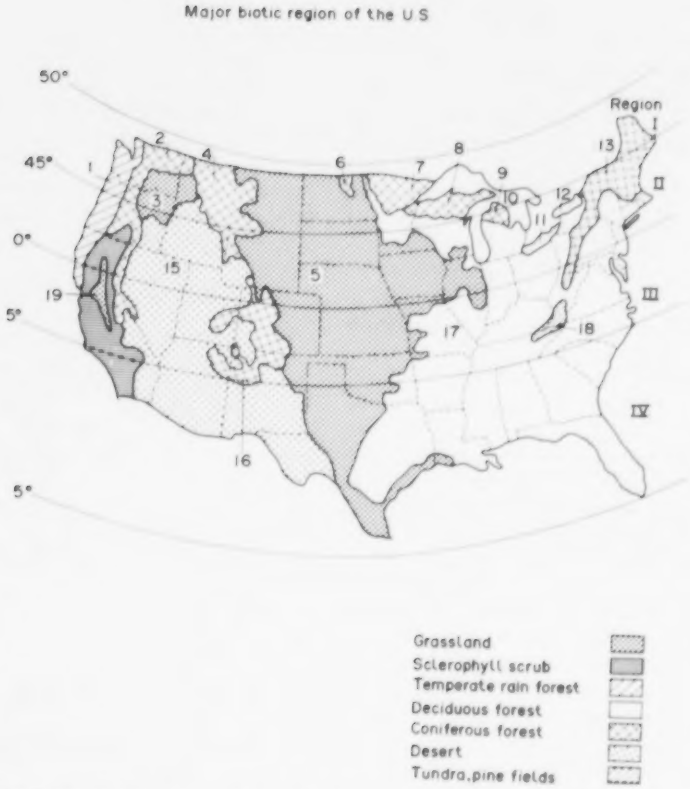


Fig. 5. Major biotic regions in the continuous United States divided into four geographical zones (from Zimmerman, 1979b).

and latitudinal differences. Isoprene emissions were assumed to be zero except in zone IV in the late fall and winter months because of the lack of leaves on deciduous trees (Fig. 3). Even in the month of July, the emissions of isoprene in zones I and II are only 3 and 18% of the emissions of isoprene in zone IV (Fig. 3). The monoterpene emissions are assumed to be very low in the late fall and winter months compared to the summer months (Fig. 4). In the month of July, the sum of the isoprene and terpene emissions in zones I and II are 15 and 34% of those in zone IV. The monthly emission rates for isoprene and monoterpenes in zone IV throughout the spring, summer, and early fall months equals or exceeds the summer emission rate in zone I.

The four zones contribute the following percentages of total annual isoprene and monoterpene emissions: zone I, 8; zone II, 15; zone III, 32; zone IV, 45. The sum of the June, July and August isoprene and monoterpene emissions constitute 58% of the annual emissions and the percentages by zone are as follows: zone I, 63; zone II, 63; zone III, 57; zone IV, 57. The June, July and August isoprene and monoterpene emissions for zone IV contribute 25% of the total annual contiguous U.S. emissions.

The isoprene emissions constitute an increasing percentage of the total emissions going from zone I to IV. For the June through August period, isoprene emissions contribute the following percentages of total emissions by zone: zone I, 5; zone II, 12; zone III, 26; zone IV, 36. The isoprene emissions in zone IV exceed the isoprene and monoterpene total emissions in zone I and are equal to the total emissions in zone II during the summer months.

Because the land areas vary from zone to zone the isoprene and monoterpene emissions are normalized to the surface areas in each zone (Fig. 5) on an annual basis is t km^{-2}. The emissions of isoprene and monoterpenes by zone are as follows: zone I (45–50° N), 0.15, 3.5; zone II (40–45° N), 0.40, 4.0; zone III (35–40° N) 1.9, 7.5; zone IV (25–35° N) 4.8, 9.2. The emissions from zone I become somewhat more significant on this basis, but are still small, particularly in terms of isoprene emissions, compared to zones III and IV.

It is clear from the previous discussion that the natural emissions are much higher in the lower latitude areas of the United States throughout the year. If natural emissions are significant compared to anthropogenic emissions, it would be most likely in rural areas in the southeastern United States in the summer months of the year.

Several significant limitations arise as a result of a

zonal–monthly average type emission computation. Each zone actually includes a diversity of biotic regions. For example, zone IV going from east to west includes deciduous forest, grassland, desert and sclerophyll scrub. The emission rates in $\mu g\ m^{-2}\ h^{-1}$ from deciduous forests (or coniferous forests) are 5–20 times higher than from grasslands or desert (Zimmerman, 1979b). Therefore, the isoprene and monoterpene emissions in the eastern portion of zone IV will be much higher than the zonal average. A second limitation is the possibility of occurrence in the summer of a period of very hot days with high light intensity in a northern zone such as zone II. For such a period of days, the emissions of isoprene and monoterpenes could be as high as in zone IV during the summer months. A third limitation results from the correctness of designation of biotic regions. For example, areas of the midwestern United States with extensive acreage of field crops such as corn are designated as grasslands. If the emission rates of natural organic volatile substances with extensive coverage by field crops in the growing season is much different than grasslands the emissions in that portion of a zone may be much different than computed by Zimmerman (1979b).

A more detailed natural emission inventory was prepared for a 60 × 81 km area including Tampa and St. Petersburg, Florida (Zimmerman, 1979a). Over 600 samples were collected using Zimmerman's enclosure technique and analyzed by gas chromatography from a variety of vegetation between April and August, 1977. The factors were computed within each 'association', i.e. pine, citrus, xeric, oak, etc. by multiplying an average emission rate for day and night by leaf biomass factors and by percentage composition for individual chemical species. The contribution of each 'association' was obtained in each land use category to give emission factors. The area of each land use category in each grid element was determined, multiplied by the area of each grid element, and summed. The daytime and night-time emissions factors were carried forward separately in this process.

The 32 land use categories were clustered into 11 types of areas. The types making the major contributions to total emissions and in parentheses the more important vegetation species contributing emissions were as follows: residential (oleander, Australian pine, sweet acadia, viburnum); pasture-rangeland (palmetto, cypress, slash pine, longleaf pine, pasture); citrus groves (orange); evergreen forest (slash pine, longleaf pine, turkey oak, live oak, laurel oak, cypress). These four types of areas contributed 93% of the total biogenic organic emissions and 97% of the isoprene and monoterpene emissions.

The total natural emissions were computed to be 157 $t\ day^{-1}$ averaged over the April–August study period (Zimmerman, 1979a). The average emission fluxes were as follows: daytime (30°C), 1710 $\mu g\ m^{-2}\ h^{-1}$; night-time (25°C), 930 $\mu g\ m^{-2}\ h^{-1}$ with a 24-h average flux of 32,000 $\mu g\ m^{-2}\ day^{-1}$. Compositionally, the daytime non-methane VOC emissions in metric tons were as follows: paraffins, 19; isoprene, 29; α-pinene, 9; β-pinene, 5; other identified monoterpenes, 5; unknown olefins, 21; 'aromatics', 15. The night-time non-methane VOC emissions in metric tons were as follows: paraffins, 14; isoprene, 0; α-pinene, 7; β-pinene, 4; other identified monoterpenes, 4; unknown olefins, 13; 'aromatics', 12. The other monoterpenes identified were myrcene, D-limonene and Δ^3-carene. It is not clear from the discussion of the analytical procedure just how unknown olefins or aromatics were specifically identified by class. The most abundant unknown was listed as unknown No. 24. The component accounted for half of the unidentified olefin. While unknown No. 24 was a very minor component in several LUDA categories, its predominate source was orange groves. This single component constituted half of the non-methane volatile organic compounds emitted by citrus groves.

Only 40% of the non-methane biogenic emissions were specifically identified. It appeared that the C_2–C_6 HCs were predominately ethane and propane. It is stated in the report that all peaks before ethylbenzene, except isoprene, benzene and toluene in the C_6–C_{12} range along with *n*-nonane and *n*-decane were considered paraffinic. However, it is unclear as to how significant the C_7 paraffins were compared to ethane and propane. Similarly, all peaks, except those associated with *n*-nonane, *n*-decane and terpenes, with longer retention times than *n*-octane were assumed to be aromatics. No explanation is given for this procedure. A number of unidentified peaks were classified as olefinic, again without explanation. Therefore, there is considerable question about the adequacy of the quantification of this large fraction of unidentified substances.

A biogenic emission inventory study was conducted in the Houston, Texas area between 16 September 1978 and 12 October 1978 (Zimmerman, 1979c). The samples were collected as previously described and analyzed by flame ionization detector-gas chromatography (Zimmerman, 1979b). The area contains three vegetation types: Bluestem prairie, oak–hickory forest and oak–hickory–pine forest. There were marked similarities with the vegetation types in the Tampa Bay study. The ground cover was estimated from 1972 aerial photographs. Fifty samples were collected from forest species, weeds, grass, leaf litter, soybean and rice and fourteen samples from fresh water, swamp and ship channel.

Hardwoods (oaks) which occupied 14% of the area emitted 1.9 $t\ h^{-1}$, while all other ground cover only emitted 0.4 $t\ h^{-1}$. Adjusting for daytime and night flux differences, isoprene was the predominant substance, contributing 70% of the 32 $t\ day^{-1}$ emitted over the 1160 km^2 area. Monoterpenes from pine and shrubs contributed 23% of the total emissions. Emissions from soil and surface waters contributed the remaining emissions, primarily as ethane and propane.

In August 1979, a biogenic emission inventory study was carried out in Pennsylvania (Flyckt *et al.*, 1980;

Lamb *et al.*, 1982). A total of 42 emission samples were obtained from isoprene-emitting hardwoods, non-isoprene-emitting hardwoods and monoterpene-emitting softwoods with additional samples collected over corn, tobacco, alfalfa, clover and mixed forage. The samples were collected by the usual Teflon bag enclosure technique and analyzed for C_4–C_{12} HCs. The sampling sites were a forested site in Hallem-Township, York County, Pennsylvania and near the city of Lancaster, Pennsylvania. The emission rate measurements were combined with biomass factors and a land use inventory to obtain an estimate of the biogenic emissions for the entire State of Pennsylvania.

For the August 1979 period, an average emission rate of 3580 tday^{-1} was computed for the State of Pennsylvania. Isoprene was the most abundant single substance identified constituting 24% of the biogenic emissions during daylight and 17% of the 24-h average biogenic emissions. There was a large number of unidentified substances present at low concentrations in emissions from hardwoods. Emissions from field crops and forage consisted of a large number of compounds, many with retention times in the same range of monoterpenes, but present at concentrations too low to permit identification. About 25% of the emissions are attributed to agricultural crops, particularly to corn. The investigators are careful to note that the HC emissions from crops are not well documented so the emission estimates could involve significant error.

The emission rates from both isoprene-emitting hardwoods and non-isoprene-emitting hardwoods showed a good log–linear relationship to temperature (Flyckt *et al.*, 1980; Lamb *et al.*, 1982). Ninety per cent or more of the variation in emission rates could be associated with temperature fluctuations. A similar relationship of emission rate with temperature was not obtained for the softwoods. Instead, the emission rate did show a good log–linear correlation with sensible heat flux.

In Table 3, isoprene and total biogenic emissions km^{-2} day^{-1} have been computed from the results of the emission studies discussed above (Flyckt *et al.*, 1980; Zimmerman, 1979a, b, c). The range of values is relatively small, particularly for total biogenic emissions, 20–49 kg km^{-2} day^{-1}. The results appear to be self-consistent within perhaps a factor of 2. However, the absolute emission rates from the U.S. emission calculation in April–August at 40 kg km^{-2} day^{-1} exceed those for the Tampa Bay area of 32 kg km^{-2} day^{-1}. As discussed earlier, the Tampa Bay area is in the portion of zone IV where the highest U.S. emission rates would be anticipated. If the Tampa Bay study results are correct, the computed emissions from the U.S. survey may tend to moderately overestimate emission rates.

The percentage of isoprene in the total biogenic emissions measured is intercompared in Table 4. The predicted percentages of isoprene from the same zone and period of year from the U.S. survey (Zimmerman, 1979b) are substantially lower than those computed from the more localized surveys in Houston (Zimmerman, 1979c) and in Pennsylvania (Flyckt *et al.*, 1980). In Tampa Bay (Zimmerman, 1979a) the isoprene also is a larger percentage of the isoprene plus monoterpenes than predicted from the U.S. survey. Since the western biotic regions tend to contain species which are poorer isoprene emitters (Zimmerman, 1979b) than eastern deciduous forests, averaging these areas into the zonal emissions should lead to underprediction of the contribution of isoprene in the specific study areas.

As discussed previously, the technique used is complex and subject to many uncertainties at each step in sampling, analysis, biomass estimate and land use survey. These studies are not entirely consistent in the approaches used to obtain the estimates for each of these factors. Considering these limitations the results are usually reasonable and are the best (and only) such estimates available.

4.2. *Measurement of the flux of biogenic hydrocarbons by micrometeorological techniques*

Micrometeorological techniques have been used to evaluate biogenic HC fluxes. The bag enclosure technique (Zimmerman, 1979b) also has been used for comparison. In a loblolly pine forest in North Carolina the flux of α-pinene was obtained by use of the energy balance/Bowen ratio technique (Arnts *et al.*, 1978; Knoerr and Mowry, 1981). Eighteen levels were instrumented to measure meteorological parameters while samples to analyze for the α-pinene were obtained at six levels above the canopy. It also is important that the vegetative surface be reasonably uniform and have a uniform fetch.

Based on this technique, the fluxes for α-pinene emissions ranged from 19 to 84 μg m^{-2} min^{-1} with half of the values between 24 and 44 μg m^{-2} min^{-1} (Arnts *et al.*, 1978). Most of the experiments were conducted between the end of June and mid-August. In a typical experiment, the α-pinene concentrations above the canopy ranged from 1.4 to 2.6 μg m^{-3}. Fluxes obtained by the bag enclosure technique were in the range of 100 to 1000 μg m^{-2} min^{-1} (Knoerr and Mowry, 1981). The higher fluxes were obtained on hot, very humid days. There was heat buildup in the bag with accumulation of water.

Another study involved measurement by a micrometeorological technique of the flux of isoprene in an oak forest in Pennsylvania (Quarles *et al.*, 1980). The atmospheric turbulent diffusivity of the isoprene was estimated by use of several relationships involving height, a displacement height, a surface roughness height, the wind speed, and temperature. Measurements were made at six levels on a tower with four levels above the canopy. A uniform fetch is also essential.

Based on this technique estimates of isoprene emissions ranged from 42.0 to 270 μg m^{-2} min^{-1} (Quarles *et al.*, 1980). The fluxes exhibited a positive logarithmic

Table 3. Comparisons of emission rates from biogenic emission inventory studies

Reference	Species	Location	Area (km^2)	Period of time	Total kg emitted (y^{-1})	kg emitted km^{-2} day^{-1}
Zimmerman (1979b)	isoprene and monoterpenes	contiguous U.S.	7.97×10^6	year	6.5×10^{10}	22
	isoprene	same	same	same	1.5×10^{10}	5.2
	isoprene and monoterpenes	same	same	April–August	4.9×10^{10}	40
	isoprene	same	same	April–August	1.2×10^{10}	9.8
	isoprene and monoterpenes	same	same	August	1.2×10^{10}	49
	isoprene	same	same	August	3.7×10^{9}	15
Zimmerman (1979a)	natural NMVOC	Tampa Bay area	4.86×10^3	April–August	2.4×10^{7}	32
	isoprene	same	same	same	4.4×10^{6}	7.2
Flyckt *et al.* (1980)	natural NMVOC	State of Pennsylvania	1.17×10^5	August	1.1×10^{8}	30
	isoprene	same	same	same	1.9×10^{7}	5.2
Zimmerman (1979c)	natural	Houston	1.16×10^3	September–October	—	28
	NMVOC	area	1.16×10^3	September–October	—	20
	isoprene	same	1.16×10^3	September–October	—	20

Table 4. Comparisons of percentage of isoprene in biogenic emissions from emission inventory studies

Survey	Location	Period of year	Percentage of isoprene
Zimmerman (1979b)	Zone II	August	10
Flyckt *et al.* (1980)	State of Pennsylvania	August	17
Zimmerman (1979b)	Zone IV	April–August	36
Zimmerman (1979a)	Tampa Bay area	April–August	47*
Zimmerman (1979b)	Zone IV	September–October	37
Zimmerman (1979c)	Houston area	September–October	70

*Percentage of isoprene plus monoterpene emissions.

relationship with temperature. The best fit isoprene concentration calculated at 6 m above the canopy averaged $7.8 \pm 3.9\ \mu g\ m_3^{-3}$. The flux values in this same study from the enclosure technique were 19.6 $\mu g\ m^{-2}\ min^{-1}$ at 20 C and 167 $\mu g\ m^{-2}\ min^{-1}$ at 30 C, while the values from the micrometeorological technique were 62.2 $\mu g\ m^{-2}\ min^{-1}$ at 20 C and 194 $\mu g\ m^{-2}\ min^{-1}$ at 30 C. The uncertainties were sufficiently large in the micrometeorological technique so the fluxes from the enclosure technique fell within these uncertainties (Quarles *et al.*, 1980).

The α-pinene flux was measured in a forest southeast of Seattle, Washington (Lamb *et al.*, 1981). This forest consisted predominately of Douglas fir. The same micrometeorological and bag enclosure techniques were used as in the study of the oak forest in Pennsylvania (Quarles *et al.*, 1980). The experiments were conducted in September–November 1980. Almost all of the individual α-pinene concentrations measured up to 8.2 m above the forest canopy were below 1 $\mu g\ m^{-3}$ with most values below 0.5 $\mu g\ m^{-3}$. Therefore, the concentrations of α-pinene measured above the Douglas fir forest (Lamb *et al.*, 1981) were much lower than the isoprene concentrations measured above the oak forest (Quarles *et al.*, 1980). The fluxes of α-pinene which ranged from 1.3 to 20 $\mu g\ m^{-2}\ min^{-1}$ were highly correlated above 60% r. h. with humidity based on the meteorological observations. Similarly, the fluxes of α-pinene from wet branches were substantially higher than from dry branches. The fluxes measured by the enclosure technique ranged from 0.15 to 11.7 $\mu g\ m^{-2}\ min^{-1}$. The flux of α-pinene appeared to be determined by the humidity in the microenvironment within the bag rather than the ambient humidity. This result (Lamb *et al.*, 1981) appears qualitatively consistent with the observation (Knoerr and Mowry, 1981) of high fluxes of α-pinene in North Carolina under hot, very humid conditions causing accumulation of water in the bag enclosures. The lower fluxes calculated from the enclosure method compared to the micrometeorological technique in this study were suggested as caused by the lower than ambient relative humidities in the bags. These results indicate the need for more concern about the microenvironment within bag enclosures and adequate measurements of this environment.

5. AMBIENT AIR CONCENTRATIONS OF NATURAL VOLATILE ORGANIC SUBSTANCES

A considerable number of studies have been carried out involving analysis of volatile organic substances at rural or remote sites. The volatile organic substances measured may be of natural origin and/or anthropogenic origin. In and near urban areas the composition of the volatile organics measured can be readily associated with vehicle exhaust emissions, gasoline evaporation to the atmosphere and losses of organic chemicals. Incineration, open burning and wood burning in fireplaces also contribute to atmospheric concentrations of volatile organic substances. In rural and remote areas such identifications with specific sources are more difficult. In some studies, investigators assumed no anthropogenic contribution would be present in a rural area.

Almost all of the analytical procedures used have depended on identification by retention time only on a chromatographic column with analysis by use of a flame ionization detector. When the large numbers of compounds which have been found in atmospheric samples are checked for retention times, often two or more compounds frequently can have the same retention time on a specific column. Therefore, it often is not possible to attribute a peak uniquely to a single compound such as α-pinene in a rural area without additional identification procedures.

5.1. *Ambient air concentrations of paraffinic hydrocarbons*

Both natural and anthropogenic sources of paraffinic HCs exist. As already discussed, methane is the major constituent of natural emissions, but smaller amounts of higher molecular weight HCs can be emitted to the atmosphere. Vehicular exhaust, and gasoline evaporation and losses of commercial natural gas are major anthropogenic sources of paraffinic HCs.

Some measurements are available which can be related to natural gas composition from seepage compared to that of commercial natural gas and vehicular emissions (Table 5) (Arnts and Meeks, 1981; Lonneman and Bufalini, 1979b; Mayrsohn and Crabtree, 1976). It is evident that the composition of commercial natural gas is substantially different from

Table 5. Source emissions composition of paraffinic hydrocarbons

Compound	Commercial natural gas Los Angeles*	Houston	Percentage Baytown Tunnel Houston†	Geogenic natural gas—Los Angeles*	Natural gas facility losses‡
Ethane	66	57	2	16	11
Propane	24	24	0.5	29	37
Isobutane	2	8	2	< 1	7
n-Butane	3	5	12	14	4
Isopentane	1	3	20	8	6
n-Pentane	1	3	9	4	5
C_6 and higher mol. wt. paraffins	3	—	55	23	36
Sum of C_4 and higher mol. wt. paraffins	10	19	84	55	52

*Mayrsohn and Crabtree (1976).
†Lonneman and Bufalini (1979).
‡Arnts and Meeks (1981).

both seepage losses and vehicular emissions. Ethane and propane dominate commercial natural gas losses. In contrast, ethane and propane constitute an insignificant portion of vehicular losses. Not only are butanes and pentanes substantial contributors to vehicular emissions, but hexanes and higher molecular weight paraffins also contribute substantially. The composition of natural gas seepage emissions obtained for Los Angeles is intermediate between commercial natural gas and vehicular emissions. While ethane and propane are important contributors to natural gas seepage, so are the butanes, pentanes, hexanes and higher molecular weight paraffins. Losses downwind of a natural gas processing facility in Colorado are also given (Arnts and Meeks, 1981). While the composition of the losses from this facility differ somewhat from the composition of seepage losses in Los Angeles, they come the closest to matching seepage composition.

Ambient air concentration measurements of paraffinic HCs at a number of rural sites are listed in Table 6. Samples from the three sites with natural gas fields nearby or in the general vicinity, Jones State Park, Texas (Seila, 1981), Rio Blanco County, Colorado (Arnts and Meeks, 1981), and Jetmore, Kansas (Martinez and Singh, 1979) all showed substantial paraffinic HC contents. The concentrations of paraffinic HCs compared to acetylene also were much higher than in vehicular exhaust at Glasgow, IL or Elkton, MO (Rasmussen *et al.*, 1976, 1977).

At the site with the highest paraffinic HC concentrations, Jones State Forest (Seila, 1981), the samples were collected at a picnic area and at a site deeper in the forest. On a percentage basis, the average paraffinic HC composition at these sites was as follows: ethane, 31; propane, 20; isobutane, 8; *n*-butane, 10; isopentane, 8; *n*-pentane, 5; hexane and higher molecular weight paraffinic HCs, 18. Comparison of these percentages with those in Table 5 suggest a mixture of seepage gas and commercial natural gas. The composition of the paraffinic HCs from the samples taken at Rio Blanco Co. (Arnts and Meeks, 1981) and Jetmore (Martinez and Singh, 1979) were somewhat different, but again the composition was not close to vehicular or commercial natural gas compositions. The lack of seepage gas emission composition measurements at these sites limits quantitative comparisons.

At the Smoky mountain site (Arnts and Meeks, 1981), use of acetylene to non-methane HC ratio was used to estimate a vehicular exhaust emission contribution ranging from 38 to 100%. However, the constituents normally associated with vehicular exhaust do not appear to be highly correlated with acetylene. The use of acetylene as a tracer of vehicular exhaust emissions may be in question owing to campfires in a nearby campground contributing to the acetylene content.

5.2. *Ambient air concentrations of isoprene and monoterpenes*

In a pioneering study, Rasmussen and Went (1965) reported on volatile organic substances in the atmosphere at rural locations. Total concentrations of volatile organic substances were reported at several rural sites in the Ozark Plateau in south central Missouri and the mountains of North Carolina in Highland, NC. Samples were analyzed with a flame ionization detector. In the winter the peaks observed in samples obtained in the Ozarks and in Holland corresponded to methane and to the components of gasoline vapors. In the summer during a 16-day period at a rural site in the Ozarks from about 7 to 14 ppb cpd of total volatile substances were observed. It was not clear whether samples were taken within the forest canopy or downwind of forested areas. During October and November two periods were observed with peak concentrations of 25 to 35 ppb cpd which corresponded to leaf drops by different groups of forest species. The authors equated summertime volatile emissions measured on their chromatographic column with plant products.

A study by Whitby and Coffey (1977) was conducted in August 1975 on Whiteface Mountain in the

Table 6. Ambient air measurements of paraffinic hydrocarbons

(Average/maximum paraffinic hydrocarbons, in ppbC)

Authors	Geographical location	Time of year	Ethane	Propane	Isobutane	*n*-Butane	Isopentane	*n*-Pentane	Sum of high mol. wt. paraffins	Sum of all paraffins measured
Rasmussen *et al.* (1976)	Elkton, Mo	21 Aug.–2 Sept. 1975	5/12	4.5/11	1.5/4.5	2.7/8.8	—	2.4/11	N.R.*	16/47
Rasmussen *et al.* (1977)	Glasgow, IL	16 July–14 Aug. 1975	5/21	5/16	1.5/11	4.5/34	—	2/10	N.R.*	18/92
Lonneman *et al.* (1978)	Central–S Florida	May 1976								
	orange groves		3/—	3/—	3/—	8/—	9/—	4/—	16/—	46/—
	everglades		2/—	0.4/—	0.3/—	0.6/—	0.9/—	0.4/—	4/—	9/—
	off shore		2/—	1/—	0.3/—	0.6/—	0.6/—	0.3/—	6/—	11/—
Martinez and Singh (1979)	Jetmore, KA	April–May 1976	21/—	10/—	3/—	8/—	3/—	4/—	N.R.*	49/—
Ferman (1981)	Keysville, VA	summer 1978	3/—	3/—	1/—	2/—	N.R.*	N.R.*	N.R.*	11/—
Seila (1981)	Jones State Forest, Texas	Jan. 1978								
	picnic area (can samples)		29/—	17/—	7/—	10/—	6/—	4/—	14/—	87/—
	forest interior (can samples)		25/—	17/—	6/—	9/—	7/—	4/—	18/—	86/—
Arnts and Meeks (1981)	Rio, Blanco, CO	July–Sept. 1978	5/6	5/6	2/3	1/2	2/2	3/10	31/51	49/80
	Great Smoky Mtn Natl. Park, TN		11/16	8/13	2/6	5/8	5/7	3/4	15/24	49/78
Cronn and Harsh (1980)	Great Smoky Mtn Natl. Park, TN	Sept. 1978	8/15	8/22	2/4	5/9	N.R.*	2/6	N.R.*	25/56

* Not reported.

Adirondack Mountains in northeastern New York. Samples were collected at altitudes from 600 m up to 1400 m between 7 and 10 August. At the higher elevations 910 m up to 1370 m, the forest consisted of balsam fir with increasing numbers of red spruce with increasing altitude. At the lowest altitude, the forest species consisted of birch, maple and scattered evergreens.

Two meters of 8% OV-101 on a diatomite support column were used for separation followed by a flame ionization detector. Seventeen chromatographic peaks were observed, excluding the C_1–C_4 HCs. A group of seven peaks were not identified, but reported to be at shorter retention times than the monoterpenes. The monoterpenes identified included α-pinene, β-pinene, *p*-cymene, and D-limonene or α-phellandrene and possibly Δ^3-carene and myrcene (Whitby and Coffey, 1977). Although the authors do not associate several peaks with any other monoterpenes, they are lumped in a 'terpene species' fraction. Therefore, the concentrations reported may represent an overestimate of the natural HCs present.

No concentrations were given for individual monoterpenes. The total concentration values are reported as $\mu g\ m^3$ (For a $C_{10}\ H_{16}$ cpd at STP 1 ppb $\simeq$ 6 $\mu g\ m^{-3}$). For a sample collected at 434 m within the forest canopy the sum of concentrations equalled 47.8 $\mu g\ m^{-3}$. The lighter non-terpene HCs in the same sample were measured at 81.8 $\mu g\ m^{-3}$. For the other samples collected on the same road, but outside the canopy, the total concentrations as 'monoterpene species' ranged from 3.5 to 32.5 $\mu g\ m^{-3}$ and averaged 16.8 $\mu g\ m^{-3}$. The concentrations of lighter compounds in the same samples ranged from 19.5 to 67.9 $\mu g\ m^{-3}$ and averaged 56.6 $\mu g\ m^{-3}$. No isoprene was identified in the lighter fraction. Therefore, over 75% of the concentrations measured outside the forest canopy were not associated with specific natural HCs. In addition, the column used could not resolve C_2–C_4 HCs. The concentrations of these HCs which often are of anthropogenic origin, were not included as 'lighter' species. It appears possible that a large part of the HCs measured was of anthropogenic origin.

Rasmussen *et al.* (1977) collected and analyzed samples in a mobile unit for HCs near the village of Glasgow, IL, 104 km NNW of the Gateway Arch in St. Louis, MO, between 17 July and 14 August 1975. The site was rural farmland primarily used for growing corn and soybeans. Analyses were made using three different gas chromatographs each containing a packed column.

Fifteen individual HCs were identified including ethane, ethene, acetylene, propane, propene, isobutane, *n*-butane, *n*-pentane, isoprene, toluene, octane, ethylbenzene, *m*- and *p*-xylene and α-pinene. Isoprene occurred at a median concentration of 3.6 ppbC and α-pinene at 0.7 ppbC (Table 7). No other monoterpene was identified. The greater portion of the HCs measured consisted of unidentified compounds. A large number of the other anthropogenic HCs known to be present in gasoline and combustion products were not identified by the procedure used in this study.

During a period of about 2 weeks from 19 August to 1 September 1975, Rasmussen *et al.* (1976) made measurements of HCs and other parameters at a rural site one km from the village of Elkton, MO (population 30) in SE Missouri on the northern edge of the Ozark Plateau about 300 km southwest of St. Louis. The site was on a farm used primarily for grazing livestock and production of corn with nearby woodland in hickory and oak. The analytical procedure and instrumentation was identical with that used by Rasmussen *et al.* (1977) outside of Glasgow, IL in the immediately preceding time period in 1975.

Isoprene was the most abundant single HC (on a weight basis) identified in the C_2–C_{10} range with a median concentration of 3.7 $\mu g\ m^3$ or 6.6 ppbC (Table 7). The peak identified as α-pinene had a median concentration of 0.2 $\mu g\ m^{-3}$ or 0.4 ppbC. No other monoterpenes were identified. The identified peaks summed up to 18 $\mu g\ m^{-3}$ or 37% of the total estimated mass. Halocarbons also were measured as tracers of urban plume intrusion into the study area. The identified compounds and some unidentified peaks were grouped as 'natural gas', aromatics, 'rural unknowns' and subjected to factor analysis to obtain correlations. Based on the statistical analysis, the authors associated 18% of the compounds with urban sources, 18% with seepage or industrial processes, 41% with rural and rural–natural and 21% was not identified as to origin. It should be noted that this statistical procedure has not been verified in any locations where most of the compounds present could be adequately identified.

Samples collected in the adjacent wooded area had considerably higher hydrocarbon concentrations on several occasions than samples collected at the trailer site on open land. These higher concentrations occurred in the afternoon and evening but not in early morning samples.

The next four studies to be described involved samples collected by Environmental Protection Agency investigators at rural sites in Massachusettes, Florida, Texas, Colorado and North Carolina. Time integrated samples were collected in Teflon bags covered with black polyethylene. The samples were shipped back to RTP, North Carolina for analysis. Analyses were performed with the flame ionization–gas chromatographic system (Seila, 1981).

HC measurements were obtained by Lonneman *et al.* (1977) at a non-urban site with oak as the major forest species at Chickatawbut Hill, the Blue Hills Reservation, outside of Boston, MA. Although isoprene has the same retention time as cyclopentane on the column used, the peak was reduced very substantially by use of a mercuric sulfate–sulfuric acid scrubber which removes olefins. Consistent with this result was the observation that during the daylight hours when isoprene is emitted from oak (Tingey *et al.*, 1979), the ratio of the peak area to that of 2-methylpentane was almost 10:1. In vehicular exhaust the ratio of

Table 7. Ambient air measurements of isoprene and monoterpenes

Authors	Geographical location/ surrounding vegetation	Sampling location(s)	Time of year	Average/maximum biogenic hydrocarbons, in ppbC				
				Isoprene	α-Pinene	β-Pinene	Δ^3-Carene	Limonene
Rasmussen *et al.* (1976)	Elkton, Missouri hardwoods and farmland	at trailer and in canopy	21 Aug.–2 Sept. 1975	6.6/30	0.4/2.5	N.R.*	N.R.*	N.R.*
Rasmussen *et al.* (1977)	Glasgow, Illinois rural farmland corn and soybeans	at trailer	16 July–14 Aug. 1975	3.6/37	0.7/2.7	N.R.	N.R.	N.R.
Lonneman *et al.* (1977)	Chackatawbut Hill Mass.; oak and other hardwoods	in clearing on top of hill	July 1975	10/34	N.R.*	N.R.	N.R.	N.R.
Lonneman *et al.* (1978)	Tampa–St. Petersburg Everglades							
	orange groves	within grove	May 1976	4/—	0.0	0.0	N.R.	0.0
	everglades	within swamp	May 1976	1/—	0.0	0.0	N.R.	0.0
	Tampa Bay area	aloft	May 1976	1/—	0.0	0.0	N.R.	0.0
Schjoldager and Wathne (1978)	Gjerdum, Norway spruce, coniferous	2 m above ground	August 1978	N.D.†	15/18	10/20	N.R.	trace
Holdren *et al.* (1979)	Moscow Mtn., north-central Idaho pine and fir	in canopy	July–Sept. 1976	trace	1.1/7.3	0.9/4.6	0.6/5.4	0.1/0.5
		(0.9) m above surface	Nov. 1976 and April 1977	trace				
		just above litter, and	July–Sept. 1976 and April 1977	trace	1.2/2.7	1.7/5.7	1.1/3.7	0.1/0.2
		above branches outside canopy	Sept. 1976	—	below 0.1	below 0.1	below 0.1	below 0.1
Zimmerman (1979)	Houston, Texas live oak	12 in (0.3 m) from branch	Sept. and Oct. 1978	4	N.R.	N.R.	N.R.	N.R.
	slash pine	6 in (0.15 m) from branch		N.R.*	2.5	0.0	N.R.	0.0
	common fig	6 inches from branch		N.R.	2	4	N.R.	N.R.
	red bay	6 inches		N.R.	7	0.0	N.R.	N.R.
Arnts and Gay (1979)	Alamance Co., NC loblolly pine	within canopy	23 Aug. 1976	N.R.*	34/56	N.R.*	N.R.*	N.R.*
			8 Sept. 1976	N.R.	15/28	N.R.	N.R.	N.R.
			7 Feb. 1977	N.R.	1.5/3	N.R.	N.R.	
			17 March 1977	N.R.	1/2	N.R.	N.R.	N.R.
		above canopy	23 Aug. 1976	N.R.	10/20	N.R.	N.R.	N.R.
			9 Aug. 1976	N.R.	3/8	N.R.	N.R.	N.R.
			7 Feb. 1977	N.R.	1/2	N.R.	N.R.	N.R.
			17 March 1977	N.R.	1/2	N.R.	N.R.	N.R.

Ferman (1981)	McKee, Kentucky	outside of	summer/76	1/3	N.R.	N.R.	N.R.	N.R.
	Keysville, Virginia	canopy	summer/76	12/150	N.R.	N.R.	N.R.	N.R
	hardwood, oak							
Quarles *et al.* (1980)	York Co. PA	5m below						
	oak	canopy top	Aug. 1979	20/30	N.R.	N.R.	N.R.	N.R.
		at canopy top		18/27	N.R.	N.R.	N.R.	N.R.
		in above canopy		20/33	N.R.	N.R.	N.R.	N.R.
		3 m above canopy		15/20	N.R.	N.R.	N.R.	N.R.
		6 m anove canopy		14/20	N.R.	N.R.	N.R.	N.R.
		12 m above canopy		11/16	N.R.	N.R.	N.R.	N.R.
Seila (1981)	Jones State Forest, TX	picnic area	Jan. 1978	0.1/—	2.8/—	N.D.†	N.D.†	N.D.†
	loblolly pine	forest canopy		0.1/—	3.0/—			
Stevens *et al.* (1981); Shaw *et al.* (1983)	Mt. Kanobili,	observatory	July 1979	7/30	8/20	N.R.	N.R.	N.R.
	Soviet Georgia	valley floor		N.D.	30/50			
	USSR	above tree canopy		N.D.	2/6			
Arnts and Meeks (1981)	Rio Blanco Co., CO	1,6 m off	24 July 1978	2.0/5.6	N.D.	N.D.	N.D.	N.D.
	sparce veg.	ground	25 July 1978					
	sage brush							
	Great Smoky Mtns.	1 m off	25 Sept. 1978	3.4/5.7	(1.0/2.2)‡	N.D.	N.D.	N.D.
	Natl. Pk. TN	ground, edge	26 Sept. 1978					
	diverse coniferous and	& low farm						
	decidious forest	forest						
Cronn and Harsch (1980)	Great Smoky Mtns	near ground	21–26 Sept. 1978	6/17	4/9	2/3	5/21	N.R.
	Natl. Pk. TN.							

* Not reported.
† Not determined, below limits of detectability.
‡ Corrected approximately for *p*-xylene content of peak.

cyclopentane to 2-methyljpentane is 1:3. Therefore, isoprene accounted for a predominate portion of the peak area. On 18 July, 1975, the concentration of isoprene averaged 10 ppbC and peaked at 34 ppbC (Table 7).

Measurements were made by Seila (1981) of the HC composition on samples collected on 4–6 January, 1978 in the Jones State Forest in Texas. The predominate vegetation nearby was loblolly pine. The samples were obtained at two sites either using Tedlar bags or stainless steel cannisters. The two biogenic hydrocarbons detected were isoprene and α-pinene. Since it was concluded that the bags were contaminated through leaks or permeation during return for analysis, only the five cannisters samples were used in tabulation of results (Table 7). The α-pinene concentration was observed to increase at sunset as the nocturnal inversion formed and the wind speed decreased, decreasing the mixing volume. The mixing height did increase somewhat during the night and increased more rapidly as the day progressed and the α-pinene concentration decreased concurrently. This diurnal profile is similar to the one predicted by Tingey (1981) for monoterpenes. Since this area was dominated by loblolly pine and the measurements were made in January, the predominance of α-pinene over isoprene is to be expected. Most of the compounds identified were typical of those either found in urban areas or were associated with seepage losses of natural gas.

Ground level and aircraft samples were collected by Lonneman *et al.* (1978) for measurement of HC composition in central and southern Florida in May 1976. Samples were collected at ground level in an orange grove in the Tampa Bay area and in the Everglades in S. Florida. Aircraft samples were collected across rural areas around Tampa–St. Petersburg and around the greater Miami area. Isoprene was not resolved from cyclopentane. The highest concentration of isoprene was observed in an orange grove. Correction for cyclopentane using the vehicular traffic ratio of 2-methylpentane to cyclopentane of three to one, reduced the values by about 1 ppbC to 4 ppbC (Table 7). The aircraft samples, after similar correction, would contain from 0 to 1 ppbC isoprene. After correction, the sample collected within the city of Miami contained only 0.5 ppbC isoprene. The isoprene constituted 5 per cent or less of the total non-methane volatile organic compounds in the samples. No detectable amounts of α-pinene, β-pinene and D-limonene were present. Of the unknown peaks listed, unknowns 2 and 3 were highest in the orange grove. Zimmerman (1979a) reported a substantial amount of an unknown olefinic compound in emissions from orange trees. A number of the other unidentified peaks were present at higher concentrations in urban than rural areas.

In the fourth study, samples were collected by Arnts and Meeks (1981) at rural sites in Colorado and in the Great Smoky Mountains. Samples also were collected in Oklahoma, but these samples were collected in Tulsa and downwind of Tulsa. No monoterpenes could be detected and isoprene ranged from 0 to 1.2 ppbC.

The natural products, α-pinene, β-pinene, camphene, D-limonene, *p*-cymene, myrcene, β-phellandrene, γ-terpinene and 1,8-cineol could not be detected in samples from any of the four sites in Colorado. In Colorado, isoprene was measured at 3.9 and 5.6 ppbC at one site, but at much lower concentrations at the other sites (Table 7). At the site where the isoprene was highest in concentration, it constituted 3–5% of the concentration of total non-methane volatile organic compounds measured at that site.

At a Smoky Mountain site, isoprene was measured in six of the nine samples at between 3 and 6 ppbC (Table 7). A peak containing both α-pinene and *p*-xylene was detectable. After correction for *p*-xylene, the α-pinene concentration was between 1 and 2 ppbC in several of the samples obtained at the Smoky Mountain site. The sum of the isoprene and α-pinene concentrations did not exceed 4–6% of the concentration of total non-methane volatile organic compounds.

Cronn and Harsch (1980) collected samples into canisters in the Smoky Mountains over a longer time period than did Arnts and Meeks (1981). The samples were subsequently analyzed by flame ionization gas chromatography. These investigators detected several terpenes not reported by Arnts and Meeks (1981). They measured the highest isoprene and α-pinene concentrations during several dry periods occurring before Arnts and Meeks began sampling.

Measurements were carried out by Holdren *et al.* (1979a) on samples collected at a forested site with mixed pine and fir on Moscow Mountain in north-central Idaho on eight days during the late summer, fall and spring months of 1976–1977. Samples were collected in stainless steel cannisters internally electropolished and in cartridges with a Tenax-GC substrate. There was a 'direct-coupled' interface of the gas chromatograph used with a Hewlett-Packard Model 5930 mass spectrometer with a dual chemical/electron ionization source. Good agreement was obtained in analyses of samples collected in the canisters with those collected on Tenax. Most of the samples were collected 3 ft (0.9 m) above the surface and outside of the forest canopy. The average concentrations and maximum concentrations are listed in Table 7.

The average percentage contribution of the four monoterpenes detected at 0.9 m above the surface and just above litter were as follows: α-pinene, 41, 29; β-pinene, 33, 41; 3-carene, 22, 27; limonene, 4, 2. The relative contributions of α-pinene and β-pinene were reversed in the two sampling locations. The variations in concentration appeared to relate best to wind speed and ventilation. No monoterpene concentrations above the detection limit of 0.1 ppbC were present outside of the canopy. Isoprene, benzene and toluene single ion peaks also are shown for a sample obtained in the forest.

Measurements of monoterpenes in a coniferous forest 25 km northeast of Oslo, Norway have been reported by Schjoldager and Wathne (1978). The forest species, pine and Norwegian spruce did not appear to emit isoprene, but α-pinene, β-pinene, and traces of limonene were identified (Table 7). Samples were collected from 2 m above ground level into wash bottles containing hexane at −20°C and samples were separated on a glass capillary chromatographic column. The monoterpenes, α-pinene and β-pinene, were present in all samples. Camphene was present in measurable quantities in a 24-h integrated sample, limonene and *p*-cymene were present as traces. One of the chromatograms was shown and it contained many large peaks before α-pinene, several unidentified peaks between α-pinene and limonene and many peaks with longer retention times than limonene.

Arnts and Gay (1979) reported diurnal variations of α-pinene within and immediately above a loblolly pine forest in North Carolina (Table 7). The α-pinene concentration peaked at 56 ppbC within the canopy on the 23 August, 1975 samples. The concentrations of α-pinene were much higher in the summer than winter samples. The concentrations were lowest during the afternoon hours and increased rapidly during the late night and early morning hours due to limited mixing within the nocturnal inversion layer.

Diurnal concentrations of isoprene have been obtained by Ferman (1981) based on real time measurements in a mobile laboratory located outside of the forest canopy. At all but one of the rural sites, isoprene levels were in the 1 to 2 ppbC range. Near Keysville, in south central Virginia, which is surrounded by hardwood forests, the isoprene concentrations during a summer study averaged 13 ppbC with a maximum over 150 ppbC (Table 7). Isoprene accounted for over 10% of the non-methane HC concentration at the Keysville site. The diurnal results displayed the expected high daylight concentrations and low night-time values. Monoterpenes apparently were identified but detailed measurements for monoterpenes are not reported.

Hydrocarbon measurements have been reported near the Abastumani Astrophysical Observatory, South Georgia, USSR (Shaw *et al.*, 1983; Stevens *et al.*, 1981). The surrounding forests were mainly pine and fir. Isoprene and/or α-pinene concentrations were reported at several locations (Table 7). A significant number of other HCs were present in the C_3–C_9 range frequently at concentrations in excess to the isoprene and α-pinene concentrations (and the other C_{10} HCs).

In summary, isoprene and α-pinene were the natural HCs most often identified. However, average concentrations of these two HCs are usually at or below 10 ppbC outside forest canopies. Maximum isoprene concentrations in the 30–40 ppbC range were reported in several studies. In one study a maximum concentration of isoprene in excess of 150 ppbC was observed (Ferman, 1981). Although as discussed earlier, higher isoprene concentrations are associated with summer daytime conditions, the exact conditions necessary to account for the highest concentrations reported is not clear.

5.3. *Ambient air concentrations of olefins and alkylbenzenes*

Olefins and alkylbenzenes which are emitted largely in urban areas also can be measured although at much lower concentrations at rural sites. The distribution of these compounds is similar to that measured at urban sites.

The anthropogenically derived olefinic HCs are present at trace concentrations which constitute a small portion of the total non-methane volatile organic compounds measured (Table 8). Ethene usually is the most abundant olefinic HC measured. In some samples ethene is next to isoprene or α-pinene in abundance as an olefinic HC. Propene is almost always present in measurable quantities. 4, 5 and 6 carbon olefins such as isobutene, *trans*-2-butene, *cis*-2-butene, 1,3-butadiene, 1-pentene, 2-methyl-1-butene, *trans*-2-pentene, *cis*-2-pentene, 2-methyl-2-butene, 4-methyl-2-pentene, 1-hexene and *trans*-3-hexene, *trans*-2-hexene and *cis*-2-hexene are frequently present above the detection limits in samples collected at rural sites (Lonneman *et al.*, 1978; Seila, 1981; Arnts and Meeks, 1981). These olefins are usually associated with vehicular exhaust emissions and gasoline evaporative losses.

The alkylbenzenes, including toluene, ethylbenzene, the xylenes, propylbenzenes, ethyl toluenes and trimethylbenzenes, have been measured in the same locations as the olefins (Table 8). Usually these alkylbenzenes are present at concentrations somewhat higher than the olefinic HCs. The alkylbenzenes have been reported at almost all of the rural/forested sites at which samples have been collected. These compounds are associated with vehicle exhaust emissions, gasoline evaporation and losses during usage of organic solvents.

Acetylene is always present in small but measurable quantities in rural/forested locations when light HC analyses are conducted (Table 8). Acetylene is known to be associated with burning vegetation but is primarily associated with vehicular exhaust emissions as well as the combustion of other fossil fuels.

5.4. *Other volatile non-methane organic compounds*

A number of peaks are almost always separable by gas chromatography which the investigators involved cannot readily identify. In the studies of Rasmussen *et al.* (1976, 1977) near Elkton, MO and Glasgow, IL, over 50% of the chromatographic peaks were not identified. In the Jones State Forest samples, on the average, about 10% was unidentified C (Seila, 1981). In Florida, on the average, the samples from an orange grove contained about 15% unidentified C, while other samples contained about 40% unidentified C (Lonneman *et al.*, 1978). In Colorado, on the average, about 30% of the carbon consisted of unidentified peaks, while on the average in the Smoky Mountain

Table 8. Ambient air measurements of alkenes, acetylene and alkylbenzenes

Authors	Geographical location	Time of year	Average/maximum concentration (ppbC) Ethene	Propene	Other l-alkenes	1,3-Butadiene and 2-alkenes	Acetylene	Alkylbenzenes
Rasmussen *et al.* (1976)	Elkton, MO	21 Aug.–2 Sept. 1975	1.8/7	0.7/1.8	N.R.*	N.R.*	0.8/1.5	>3/15
Rasmussen *et al.* (1977)	Glasgow, IL	16 July–14 Aug. 1975	2.6/15	0.7/3	N.R.	N.R.	1.1/6	I.D.†
Lonneman *et al.* (1978)	Central–S. Florida	May 1976	3.5/—	1/—	2.5/—	2/—	4.5/—	25/—
	orange groves		0.7/—	0.6/—	0.0/—	3.5/—	1.2/—	26/—
	everglades		0.3/—	0.4/—	0.4/—	/—	0.9/—	12/—
	Tampa Bay area							
Martinez *et al.* (1979)	Jetmore, Kansas	April–May 1978	0.8/—	0.8/—	N.R.	N.R.	N.R.*	N.R.*
Seila (1981)	Jones State Forest Texas	Jan. 1978						
	picnic area		4/—	1/—	1/—	2/—	3/1	15/—
	forest interior		6/—	4/—	3/—	2/—	2.5/—	34/—
Ferman (1981)	Keysville, VA	summer 1976	0.3/—	N.R.	N.R.	N.R.	0.9	N.R.
Arnts and Meeks (1981)	Rio Blanco Co., Colorado	July 1978	1.5/—	1/1	1/2	2/3	2/3	22/26
	Great Smoky Mtn. Natl. Pk. TN	Sept. 1978	4/7	2/8	1/2	2/6	5/7	20/26

* Not reported.
† Insufficient data.

samples, about 15% of the C was associated with unidentified peaks (Arnts and Meeks, 1981).

Urban ambient air measurements include a large number of individual higher molecular weight paraffinic and aromatic HC compounds in the air derived from gasoline and vehicular exhausts (Lonneman *et al.*, 1974, 1979). Nevertheless, many HCs identified in gasoline and vehicular exhaust analyses (Sanders and Maynard, 1968; Dimitriades *et al.*, 1972) are not included in gas chromatographic HC analyses of samples from urban and particularly from rural sites. Comparisons of the HCs identified by a gas chromatographic procedure used in a number of urban (Lonneman *et al.*, 1974, 1979) and rural studies (Arnts and Meeks, 1981; Lonneman *et al.*, 1978; Seila, 1981) with those measured in gasoline and vehicular exhaust analyses (Sanders and Maynard, 1968; Dimitriades *et al.*, 1972) indicates that 20–30% of the HCs emitted from these sources are not identified in the ambient air analyses. A similar comparison with the gas chromatographic procedures used by Rasmussen *et al.* (1976, 1977) indicates that 40–60% of the HCs emitted from vehicles and gasoline evaporation were not identified in the ambient air samples. These results suggest that a large number of minor anthropogenic components can be present at rural sites, but not reported probably because they occur at or below the limits of detectability.

A portion of the unidentified peaks may be associated with biogenic compounds. However, in several of the rural studies (Arnts and Meeks, 1981; Lonneman *et al.*, 1978; Seila, 1981), the authors specifically state that they did not observe any other of the monoterpenes identified in the emissions from individual biogenic sources (Zimmerman, 1979a, b).

6. LIFETIMES OF VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE

The lifetimes of many volatile organic compounds in the atmosphere are determined predominantly by their rates of reaction with hydroxyl radicals and, if olefinic HCs, their rates of reaction with O_3 (Altshuller, 1980). The atmospheric concentrations of hydroxyl radicals can vary over a wide range depending on availability of solar radiation. Local meteorological conditions and time of the day as well as latitude and season determine the concentrations of this radical. Radicals disappear rapidly at night, so at night-time and at very low solar intensities hydroxyl radical concentrations will approach zero.

O_3 varies less with changes in environmental parameters than hydroxyl radicals. O_3 concentrations at rural sites can range over a factor of 10 (Martinez and Singh, 1979).

As a result of the variability in the concentrations of OH and O_3, no unique lifetimes can be assigned to individual volatile organic compounds. Nevertheless, several typical conditions can be considered so as to estimate the lifetimes for various HCs.

The rate constants needed to compute the lifetimes of a group of representative HCs including the monoterpenes are listed in Table 9. The literature values (Arnts and Gay, 1979; Grimsrud *et al.*, 1975; Huie and Herron, 1975; Pate *et al.*, 1976; Pitts *et al.*, 1977b; Stedman *et al.*, 1973) have been converted to units of $ppm^{-1}\,h^{-1}$. The rates of reaction of paraffinic HCs, acetylene and alkylbenzenes with O_3 are very slow. The rates of reaction of O_3 with olefinic HCs are much faster, and these rates vary with the structure of the olefin over a wide range (Table 9). The rates of reaction

Table 9. Rate constants for reactions of selected hydrocarbons with ozone and hydroxyl radicals

Hydrocarbon	K_{O_3+HC} ($ppm^{-1}\,h^{-1}$)	K^{b}_{OH+HC} ($ppm^{-1}\,h^{-1}\times10^{-5}$)
Ethane	0[a]	0.25
n-Butane	0[a]	2.6
3-Methylpentane	0[a]	6.3
Acetylene	0.003[c]	0.15
Ethylene	0.15[d,e]	6.9
Propene	1.0[d,e,g]	22
2-Methylpropene	1.15[e,f]	45
trans-2-Butene	20[d,e]	62
2-Methyl-2-butene	35[e]	71
Isoprene	1.1[g]	69
α-Pinene	13[f]	52
β-Pinene	3.2[f]	60
Δ^3-Carene	11[f]	76
β-Phellandrene	16[f]	103
D-Limonene	58[f]	132
Myrcene	112[f]	201
Toluene	1×10^{-5}[c]	5.3
m-Xylene	5×10^{-5}[c]	21
1,3,5-Trimethyl-benzene	2×10^{-4}[c]	43

[a] Extremely slow; [b] Pitts *et al.* (1977b); [c] Pate *et al.* (1976); [d] Stedman *et al.* (1973); [e] Huie and Herron (1975); [f] Grimsrud *et al.* (1975); [g] Arnts and Gay (1979).

of hydroxyl radicals vary with structure of the HCs over almost a factor of 1000.

Using the values for the rate constants in Table 9, the daylight life-times have been computed for four typical conditions: a July midday concentration at 25–45°N latitude of 10^{-7} ppm of OH and 8×10^{-2} ppm of O_3; an April or October average diurnal concentration at 35°N latitude or a July average diurnal concentration at 55°N latitude, of 10^{-8} ppm of OH and 5×10^{-2} ppm of O_3; and a January average diurnal concentration at 45°N latitude or a January midday concentration at 55°N latitude of 10^{-9} ppm of OH and 2×10^{-2} ppm of O_3 and a summer night-time with 5×10^{-2} ppm of O_3. The appropriate OH radical concentration was taken from tabulated values (Altshuller, 1979) and the corresponding ozone concentrations estimated as those likely to be associated with the OH concentration assumed. The lifetimes in Table 10 were computed from the rate constants and these values of OH radical and O_3 by use of the kinetic relationship $T = [(K_{O_3}C_{O_3}) + (K_{OH}C_{OH})]^{-1}$.

The lifetimes increase substantially with decreasing concentrations of ozone and hydroxyl radical. These lifetimes range from fractions of 1 h for some of the olefinic HCs under more reactive conditions to months to years for paraffinic HCs under the least reactive conditions. Ethane and acetylene react extremely slowly under all of the atomospheric conditions.

There are significant overlaps in lifetimes between groups of HCs. The lifetimes of anthropogenic olefins associated with vehicular exhaust and gasoline evaporation, such as *trans*-2-butene and 2-methyl-2-butene, overlap with the more reactive monoterpenes, Δ^3-carene, β-phellandrene and D-limonene. Similarly, less reactive anthropogenic olefins represented by 2-methylpropene have lifetimes about the same as isoprene. For summer midday conditions the alkylbenzenes have lifetimes in the same range as olefins such as ethylene, propene and methyl propene. The higher molecular weight paraffinic hydrocarbons from *n*-butane to 3-methylpentane have lifetimes in the same range as the less reactive alkylbenzenes, as represented by toluene.

The rates of reaction of O_3 with paraffinic HCs and with alkylbenzenes are negligible. Since the lifetimes of these classes of compounds depend on the OH radical concentrations, their lifetimes become extremely large at night and for other low light intensity conditions. The lifetimes of several HCs such as ethene, propene, 2-methylpropene and isoprene change substantially with the variations in concentrations of O_3 and hydroxyl radicals. As hydroxyl radical concentrations decrease, the lifetimes of these HCs increase rapidly. In contrast, the lifetimes of olefinic HCs such as *trans*-2-butene, 2-methyl-2-butene, α-pinene, Δ^3-carene, β-phellandrene, D-limonene and myrcene under varied atmospheric conditions are only moderately dependent of OH radical conditions in the atmosphere. As a result, the lifetimes of this group of HCs vary more slowly than the less reactive olefinic HCs. At night, these types of olefinic HCs continue to be consumed at substantial rates by excess O_3 remaining from the day before. However, paraffinic HCs, acetylene, and aromatic HCs are inert, while ethene, propene, 2-methylpropene and isoprene do not undergo *substantial* reductions in concentration owing to chemical removal at night.

Table 10. Lifetimes (h) of hydrocarbons in atmosphere in presence of ozone and hydroxyl radicals

Hydrocarbon	$[O_3] = 0.08$ ppm $[OH] = 10^{-7}$ ppm*	$[O_3] = 0.05$ ppm $[OH] = 10^{-8}$ ppm†	$[O_3] = 0.02$ ppm $[OH] = 10^{-9}$ ppm‡	$[O_3] = 0.05$ ppm $[OH] = 0$§
Ethane	400	4,000	40,000	inert
n-Butane	38	380	3,800	inert
3-Methylpentane	16	160	1,600	inert
Acetylene	574	3,300	13,300	6,600
Ethene	12.3	69	270.0	133
Propene	3.3	14.0	46.0	20
2-Methylpropene	1.8	9.1	32.0	15.0
trans-2-Butene	0.5	0.9	2.5	1.0
2-Methyl-2-butene	0.3	0.6	1.4	0.6
Isoprene	1.3	8.1	34.0	18.0
α-Pinene	0.6	1.4	3.8	1.5
β-Pinene	1.1	4.6	14.0	6.3
3-Carene	0.6	1.6	4.4	1.8
β-Phellandrene	.4	1.1	3.0	1.2
D-Limonene	0.2	0.3	0.8	0.3
Myrcene	0.1	0.2	0.4	0.2
Toluene	19.0	190	1900	inert
m-Xylene	4.8	48	480	inert
1,3,5-Trimethyl-benzene	2.3	23	230	10,000

* July midday concn 25–45°N, daylight lifetime.
† April/October av. diurnal concn 35°N or July av. diurnal concn, 55°N, daylight lifetime.
‡ Jan av. diurnal concn 45°N or Jan midday concn 55°N, daylight lifetime.
§ Summer night-time concn, night lifetime.

7. AMBIENT AIR REACTION PRODUCTS OF ANTHROPOGENIC AND BIOGENIC VOLATILE ORGANIC COMPOUNDS

Both anthropogenic and biogenic volatile organic compounds can participate in the same types of atmospheric reactions (Altshuller and Bufalini, 1965; Arnts and Gay, 1979). Almost all volatile organic compounds will react in the presence of solar radiation at varying rates with NO_x to convert NO to NO_2 which subsequently reacts to form nitric acid and peroxyacyl nitrates. O_3 is produced as a product. The volatile organic compounds react with hydroxyl radicals and O_3 to form other radicals and stable products including a variety of volatile oxygenated organic compounds. Although the general details of such reactions are similar, differences in initial composition and rates of reaction can result in somewhat different yields of the same products. Other more unique products will be formed from those organic compounds with specific structural characteristics (Altshuller and Bufalini, 1965; Arnts and Gay, 1979). Organic aerosols can be produced from the solar-induced reactions of higher molecular weight olefins and alkylbenzenes with NO_x (Altshuller and Bufalini, 1965; Grosjean, 1977).

7.1. *Ozone formation*

The potential of individual volatile organic compounds to participate in atmospheric O_3 formation can be estimated in a number of ways. A conventional approach used to estimate the potential for O_3 formation involves plots of O_3 yields for various individual volatile organic compounds over a range of volatile organic compound to NO_x ratios (Altshuller and Bufalini, 1965). For many types of volatile organic compounds, as volatile organic compound to NO_x ratios increase from very low values, O_3 yields increase. O_3 yields maximize at an optimum ratio, followed by a rapid decrease in O_3 yield at high organic compound to NO_x ratios. This type of behavior has been observed for olefins, including the monoterpenes. Arnts and Gay (1979) found the O_3 yields of propylene to be higher than those for isoprene and monoterpenes throughout a wide range of olefin to NO_x ratios. The O_3 yields of the monoterpenes drop off rapidly at high ratios because of the rapid consumption of O_3 formed by reaction with the monoterpene. Kaiserman and Corse (1981) also reported low ozone yields at the high end of the ratio range from 70:1 to 210:1 of ppm carbon to NO_x. These investigators also reported that the O_3 yields of α-pinene–NO_x and β-pinene–NO_x systems were insensitive to relative humidity.

Kamens (1981) has discussed a series of solar irradiation experiments in a dual chamber system in which 20% α-pinene on a ppmC basis was either substituted for or added to a simulated urban HC mixture. The results of the substitution and additional experiments indicated that the O_3 yields to be expected from α-pinene were very nearly the same as for an equal C content of the urban mixture. In other experiments, α-pinene substituted for part of the urban mixture and was allowed to react with O_3 for 2 h in the dark to form reaction products before adding the urban mixture to the two sides of the chamber. In some experiments substitution of α-pinene resulted in the same O_3 yield while other experiments indicated a possible reduction in ozone yield.

One useful parameter for evaluating O_3 production involves calculating the ratio of O_3 formed to the amount of volatile organic compound consumed over the same time period in smog chamber experiments. The period selected is to the time of O_3 concentration maximum if it occurs, or to the end of the irradiation period. Arnts and Gay (1979) have provided results of this parameter for propylene, isoprene, α-pinene, D-limonene and *p*-cymene over a range of HC to NO_x ratios. Pitts *et al.* (1977a, 1979) have obtained measurements which can be used to make similar computations for *n*-butane, 2,3-dimethyl butane, ethene, propene, toluene, *m*-xylene, formaldehyde and acetaldehyde. The computed values of O_3 (ppm vol) produced per ppmC of volatile organic compound consumed are listed in Table 11. The HC concentrations in these studies frequently were in the 1–10 ppbC range well above ambient concentrations of individual HCs.

In order to evaluate the significance of these laboratory results in rural atmospheres, the range of volatile organic compounds to NO_x ratios at rural sites needs to be estimated. One field study which includes some measurements of both volatile organic compounds and NO_x was conducted in the Ohio Valley area in the summer of 1974 (Research Triangle Institute, 1975). The mean of hourly concentrations of NO_2 total HCs, and methane are available for each hour of the day at sites outside of Wilmington, Ohio, McConnelsville, Ohio and Wooster, Ohio. The ratios of total HC minus methane divided by NO_2 in ppmC to ppm NO_2 were reported as follows: Wilmington, Ohio, 13; McConnelsville, Ohio, 53; Wooster, Ohio, 42. In data analysis (Martinez and Singh, 1979) of the subsequent SURE study results for 1977, mean NO_x concentrations ranging from 5 to 15 ppb and NO to NO_x ratios of 0.1 to 0.3 were obtained for rural and rural–suburban sites. Using a ratio of 0.2, the corresponding $NO + NO_2$ to NO_2 ratio would be 1.25. Therefore, the total HC to NO_x ($NO + NO_2$) ratios were in the 10–40:1 range.

The measurements from the 1974 study (Research Triangle Institute, 1975) and the 1977 study (Martinez and Singh, 1979) indicate mean NO_x levels of 7–13 ppb and of 5–15 ppb (excluding suburban sites). Measurements of HC at various sites by gas chromatography give VOC concentrations usually between 50 and 200 ppbC (Arnts and Meeks, 1980; Lonneman, 1977; Lonneman *et al.*, 1975; Seila, 1981). Taking the extreme values a range of ratios between 10:1 and 40:1 is estimated. Therefore, a range of ratios of 10:1–40:1 will be assumed as applicable in the mixed layer over rural sites in the midwestern and eastern United States.

Table 11. Ratios of ozone produced to volatile organic compounds consumed in simple mixtures

Volatile organic compound	Ratios of VOC to NOX 4:6	8:11	14:18	23:27	35:45	55:75
n-Butane*	ND	ND	0.05	0.07	0.1	(0.15)‡
2,3-Dimethylbutane*	ND	ND	ND	0.19	0.20	ND
Ethene*	0.41	0.39	0.28	ND	ND	ND
Propene*	0.20	0.21	0.27	0.15	ND	ND
Toluene*	ND	0.15	0.09	0.07	0.15	0.08
m-Xylene*	0.18	(0.15)‡	0.16	ND	ND	ND
Propene*	0.43	0.24	(0.18)‡	(0.12)‡	0.08	(0.06)‡
Isoprene†	0.30	0.19	0.12	0.09	(0.07)‡	0.04
α-Pinene†	(0.2)‡	0.18	0.08	(0.06)‡	0.04	0.015
D-Limonene†	0.15	0.12	(0.09)‡	0.03	0.014	<0.01
p-Cymene†	0.6	0.19	0.16	(0.12)‡	0.08	(0.08)‡
Formaldehyde*	ND	ND	0.70	ND	ND	ND
Acetaldehyde*	ND	0.55	ND	ND	ND	0.25

* Pitts *et al.* (1977a, 1979).
† Arnts and Gay (1979).
‡ Interpolated values.

As can be seen from the results in Table 11, there is a substantial variation in the efficiencies in O_3 production over a range of ratios of volatile organic compounds to NO_x. At the lower ratios, 8–11, olefins when irradiated with NO_x are very effective in the reactions producing O_3. As the ratios increase, the efficiencies for O_3 production associated with the olefins decrease rapidly. The decrease occurs because of increasing consumption of O_3 by the increasing concentrations of olefin. Irradiations of nitrogen oxides with volatile organic compounds which do not react at significant rates with O_3 do not show decreases in efficiency of participation in O_3 production with variations in reactant ratios. The paraffinic HCs and alkylbenzenes which are somewhat less efficient that the olefins near the lower end of the atmospheric ratio range are more efficient near the upper end of the atmospheric ratio range of volatile organic compounds to NO_x (Table 11).

The O_3 producing potential for compounds averaged over this range are as follows: propene, 0.15; isoprene, 0.12; α-pinene, 0.09; D-limonene, 0.06; *p*-cymene, 0.11 and toluene, 0.12. For compounds with less complete experimental results, the estimated average potentials are as follows: *n*-butane, 0.07 or less; 2,3-dimethyl-butane, 0.2 or less; ethene, 0.3 or less and *m*-xylene, 0.15 or less. Thus, the paraffinic HCs, *n*-butane and 2,3-dimethyl-butane, and the aromatic HCs, toluene, *m*-xylene and *p*-cymene have average O_3-producing potentials in this range equal to or greater than those of the olefinic HCs with shorter ambient air lifetimes.

O_3-producing potentials also can be computed from the measurements of Pitts *et al.* (1979) on mixtures of 7 HC components with NO_x. The experiments are listed in Table 12 by composition and for mixtures of the same composition with increasing HC to NO_x ratios. If the experiments in each of the four subsets with

Table 12. Ozone produced to volatile organic compounds* consumed in multicomponent HC–NO_x mixtures

Run	Percentage composition Paraffin†	Olefin‡	Alkylbenzene§	Sum of HC in ppmC	NO_x ppm	Ratio HC:NO_x	Peak or Max O_3	O_3: $\Sigma\Delta$HC
232	87	8	5	9.31	0.49	19:1	0.31	0.10
246	87	8	5	8.56	0.56	17:1	0.57	0.16
233	87	8	5	9.50	0.10	92:1	0.33	0.12
241	63	24	13	4.95	0.49	10:1	0.41	0.24
238	63	24	13	10.07	0.95	10:1	0.69	0.15
237	65	22	13	10.46	0.48	22:1	0.65	0.18
231	67	20	13	13.17	0.49	27:1	0.62	0.12
247	26	39	36	6.12	0.50	12:1	0.65	0.22
245	25	38	37	12.86	0.99	13:1	0.89	0.16
242	27	37	36	12.83	0.50	25:1	0.67	0.16
243	28	48	24	9.74	0.50	19:1	0.71	0.24

* Pitts *et al.* (1979).
† *n*-Butane and 2,3-dimethylbutane.
‡ Ethene, propene and *t*-2-butene.
§ Toluene and *m*-xylene

differing HC compositions are averaged, the ozone produced per ppmC of HC consumed increases slowly with decreasing paraffin content and increasing olefin and alkylbenzene content. The parameter O_3:$\Sigma\Delta HC$ averages 0.13 for 87% paraffin in content, 0.17 for 63–67% paraffin content, 0.18 for 25–27% paraffin content. The single experiment, 243, with low paraffin content and the highest olefin content gave a O_3:$\Sigma\Delta HC$ of 0.24. However, there also is an indication of an influence of initial concentration on O_3:$\Sigma\Delta HC$. The two experiments, 241 and 247, with the lower initial hydrocarbon concentrations have the larger values for O_3:$\Sigma\Delta HC$. If these two experiments are excluded, the trend with changing composition among the subsets average 0.13, 0.15, 0.16 and 0.24. Thus, the spread in values of O_3:$\Sigma\Delta HC$ tend to decrease with increasing complexity of the HC mixtures.

The parameter, O_3:$\Sigma\Delta HC$, in the previous computations has been obtained near or at the maximum formation rate for O_3 in the experiments considered. This parameter also has been computed hour by hour for a number of experimental irradiations. The peak values of O_3:$\Sigma\Delta HC$ proved to be 1.2–1.6 times larger than the average values for an experiment.

There is a tendency for O_3:$\Sigma\Delta HC$ to increase at a specific volatile organic compound to NO_x ratio as the concentration of the reactants decreases. This effect is shown in Table 13 for several single and multicomponent VOC mixtures. The average O_3:$\Sigma\Delta HC$ values given are computed from the measurements of Pitts *et al.* (1979). Such a result suggests that efficiencies of ozone production at ambient air concentration levels which are lower than in these laboratory experiments may be somewhat higher than estimated in Table 12.

7.2. *Potential for formation of aerosols*

The ability of volatile organic compounds to participate in atmospheric reactions with NO_x to form aerosols is much more variable than is their ability to participate in the formation of O_3. Cyclic olefins such as cyclohexene and α-pinene are highly effective in forming organic aerosols while aromatic HCs and the acyclic olefins, particularly C_7 and higher olefins are moderately effective producers of organic aerosols (Altshuller and Bufalini, 1965; Grosjean, 1977). Paraffinic HCs, acetylenic HCs, lower molecular weight olefins, aldehydes and other oxygenated and halogenated compounds have low to negligible effectiveness in forming organic aerosols. While higher molecular weight diolefins have been shown to form large yields of aerosols (Grosjean, 1977), lower molecular weight diolefins such as isoprene have not been demonstrated to be significant producers of organic aerosols (Kamens *et al.*, 1981). Laboratory studies providing measurements of aerosol products are available for reactions of O_3 and/or NO_x with volatile organic compounds such as cyclohexene, α-pinene, β-pinene, limonene, terpinolene and toluene (Grosjean, 1977; Hull, 1981; Schuetzle and Rasmussen, 1978; Schwartz, 1974).

An estimate of organic aerosol-forming ability relative to cyclohexene set at 100, derived from various studies has been summarized from various smog chamber studies (Grosjean, 1977). Relative to cyclohexene, values for paraffins, acetylene, aldehydes, and lower molecular weight olefins are well below 10. For aromatics, most of the values, if Miller *et al.* (1972) results are considered also, range between 10 and 30. The 6 and 7 carbon olefins have values ranging between 5 and 10 with a few lower values. Cyclopentene has an average value around 65 and α-pinene around 160 (Grosjean, 1977). The 6 carbon and higher diolefins have high values, but these compounds have never been identified in sources or the ambient air. The accuracies of estimates of aerosol-forming ability based on single HC–NO_x systems are limited by apparent inhibition effects in mixtures of HCs with NO_x (Miller *et al.*, 1972).

A detailed study of aerosol formation from irradiation of a 17-component HC mixture with NO_x is

Table 13. Variations in ratios of ozone produced to volatile organic compounds consumed with concentration of reactants*

No. of expts	Hydrocarbon Compd	Average concn (ppmC)	Average HC:NO_x	Average O_3:ΔHC
1	*n*-butane	1.52	11	0.27
2		8.50	15	0.05
1		15.7	12	0.005
1	toluene	1.47	15	0.20
5		7.57	16	0.09
1		13.2	13	0.06
2	propene	0.28	2.3	0.60
13		1.54	2.9	0.28
		3.12	2.8	0.18
1	7 component	4.95	10	0.24
1	(63, 24, 13)	10.1	10	0.15
1	7 component	6.12	12	0.22
	(26,39,36)	12.9	13	0.16

* Pitts *et al.* (1979).

available (Miller and Joseph, 1976). At higher NO_x concentrations, there is suppression of aerosol formation. Increases in HC concentration at low NO_x concentrations result in a rapid increase in aerosol volume followed by a leveling off to a plateau. At higher NO_x concentrations, the effect of increased HC concentration on increase in aerosol volume was more gradual. At fixed HC to NO_x of 5:1 and 10:1, the aerosol increased rapidly at lower concentration levels of reactants and more slowly at higher concentrations of reactants. The lowest concentration mixtures, which were within the ambient air range, produced two-thirds as much aerosol as the high concentration mixtures. Thus, the lowest concentration mixtures investigated were capable of producing substantial amounts of organic aerosols.

7.3. *Volatile organic products formed by reactions of biogenic HCs*

A large number of volatile organic products are formed by the reactions in ultraviolet irradiations of biogenic HCs with NO_x (Arnts and Gay, 1979). The lower molecular weight products formed include formaldehyde, acetaldehyde, formic acid, acetone and peroxyacetyl nitrate (Table 14). These lower molecular weight products account for less than 10% of the reacted monoterpenes. These products are not unique to isoprene or monoterpenes. These same products are formed in high yields from anthropogenic HCs such as ethene, propene, *trans*-2-butene, 2-methyl-2-butene, and in lower yields from alkylbenzenes and other anthropogenic HCs (Altshuller and Bufalini, 1965).

The volatile organic products, methacrolein and methyl vinyl ketone, appeared to be specific to isoprene (Arnts and Gay, 1979). These compounds and the lower molecular products discussed above account for 30–45% of the reacted isoprene. However, in more recent work 73% of the reacted isoprene has been accounted for as methacrolein (33%), formaldehyde (19%), methyl vinyl ketone (15%) and CO (6%) (Kamens *et al.*, 1981) also. Trace amounts of acetaldehyde, methylglyoxal, propene, and possibly ketone were observed. Monoterpenes in gas phase ozonolysis form a number of higher molecular weight products which maintain the bridge structure of the monoterpenes (Hull, 1981). Since the known anthropogenic HCs do not have this structure, products containing it may be considered specific to the monoterpenes. Such products include compounds such as *cis*-pinonic acid which is likely to be in aerosol form, but other products identified such as nopinone, 3-hydroxy nopinone, *cis*-pinonaldehyde and other related compounds have vapor pressure which would result in their occurring as vapors in the ambient atmosphere. These 10 carbon volatile oxygenated products at least for α-pinene and β-pinene appear to account for most of the reacted monoterpene.

Cronn *et al.* (1977) identified pinonic acid, norpinoic acid and several other isomers as tentative products of terpenes in a sample collected in West Covina, CA. The sum of concentrations of aerosols tentatively identified as products of terpenes summed to about 1 $\mu g\ m^{-3}$. In comparison, the sum of all of the organic aerosols measured in the same sample was 37 $\mu g\ m^{-3}$ and the sum of all inorganic aerosols measured was 45 $\mu g\ m^{-3}$. Therefore the aerosol products of terpenes account for about 1% of the aerosol concentrations.

Mass spectrometry analysis was carried out on aerosol samples collected near the Abastumani Astrophysical Observatory on the peak of Mt. Kanolili in Soviet Georgia (Shaw *et al.*, 1983). Some evidence for the presence of pinonic acid or pinonaldehyde as well as ozonized limonene compounds was obtained from the abundancies of oxygen-containing ions.

8. GENERAL DISCUSSION

Based on the previous discussion several issues can be identified which require further consideration.

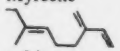
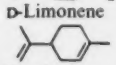
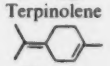
8.1. *What are the relationships between anthropogenic and biogenic emission inventories and air quality measurements?*

The biogenic inventory developed by Zimmerman (1979b) and discussed earlier, estimated on an annual basis that 15 Mt of isoprene and 50 Mt of monoterpenes are emitted from the entire contiguous United States (Table 3). For the month of July, the peak month for biogenic emissions, the isoprene emissions were computed to be 3.7 Mt and the monoterpene emissions were computed to be 11 Mt.

The anthropogenic emissions for the United States have been estimated to total 27 Mt (U.S. Environmental Protection Agency, 1974) with vehicular emissions contributing about 12 Mt y^{-1} in 1977 (Radian Corporation, 1978; Mann, 1981). Monthly inventories of anthropogenic emissions are not available, but it seems reasonable to assume no large variations from month to month. Assuming July anthropogenic emissions are 1/12 the annual emissions, the anthropogenic emissions would total 2.3 Mt and the vehicular emissions 1 Mt. The annual ratio of biogenic to anthropogenic emissions would be 2.4:1 and the annual ratio of biogenic emissions to vehicular emissions would be 5.1:1. Considering biogenic emissions of isoprene to vehicular emissions, the annual ratio would be 1.2:1 and the ratio in July would be 3.7:1.

Comparisons can be made between these ratios of biogenic to anthropogenic emissions with the corresponding ratios obtained from ambient air quality measurements in rural areas. An approach which would tend to compensate for differences in atmospheric reaction rates would involve comparison of the biogenic HC, isoprene, with an anthropogenic HC which reacts at about the same rate as isoprene in the atmosphere. Propene appears to be a suitable choice based on its atmospheric rate of reaction and avail-

Table 14. Reactivity and products by long infrared at 60 min (from Arnts and Gay, 1979)

Compound	C/NO_x ratio	%HC reacted	H_2CO	HCOOH	CO	CO_2	CH_3CHO	PAN	$(CH_3)_2CO$	Total ppmC products	% Carbon accounted for
Isoprene	31	68	2.39	0.44	0.77	0.2	2.0	0.32	0	8.44	31
	10*	100	6.8	3.4	4	2.0	1.95	1.2	0	32.8	44
Myrcene	62	73	0.84	0.16	0.26	0.24	2.35	0.70	0.76	9.88	17
											
D-Limonene	67	91	0.9	0.35	0.46	0.49	0.23	0.24	0	3.14	4
											
Terpinolene	62	95	1.2	0.31	0.49	0.69	0.35	0.28	0	3.95	5
											
α-Pinene	67	72	0.33	0.32	0.39	0.6	1.57	0.20	0	5.18	9
β-Pinene	53	58	0.94	0.39	0.23	0.4	0.05	0.018	0	2.58	6
Δ^3-Carene	67	60	0.46	0.39	0.50	0.9	0.33	0.26	0	3.43	7

Initial hydrocarbon concn = 8 ppm. Products as ppm compound (v/v). $k_d(NO_2) = 0.51\ min^{-1}$.

* Initial concentrations: 15 ppm isoprene, 7.5 ppm NO_2; irradiated for 45 min; additional products detected; 1.0 ppm methacrolein, 1 ppm methyl vinyl ketone, 0.5 ppm HNO_3, 1.1 ppm 0_3, 0.5 ppm NO_2 (remaining).

ability of ambient air measurements for propene at rural sites.

Propene constitutes 4 to 5% of the vehicular emissions (Dimitriades *et al.*, 1972; Lonneman *et al.*, 1974, 1979; Sanders and Maynard 1968). Multiplication of the vehicular emissions of 12 t by 0.05, results in propene emissions of 6×10^5 t y^{-1} (not adjusted for evaporative emissions). Since the annual U.S. emissions of isoprene were computed as 15×10^6 t y^{-1}, the ratio of isoprene to propene would be 25 to 1. The ratios of isoprene to propene also can be computed for the months of May, July, August and September when the sampling was conducted at the rural sites. Propene is assumed to be emitted in equal amounts each month of the year, so its emissions would be 5×10^4 t per month. The monthly isoprene emissions for May, July, August and September from Zimmerman (1979b) would be 1.5×10^6, 3.7×10^6, 3.7×10^6 and 2.0×10^6 t per month. Therefore, the ratios of isoprene to propene emissions are as follows: May, 30; July, 74 and September, 40. It would be desirable to adjust these ratios to specific geographical locations, but the necessary information is not available. Since all of the rural sites to be considered are in zones III and IV, the isoprene emissions should equal or exceed U.S. averages on a per km^2 basis (Table 3).

Within the limitations of the assumptions discussed above, the ratios of the isoprene to propene ambient air concentrations (Tables 7 and 8) compared to the ratios from the emission inventory estimates made above are by site as follows: Elkton, MO (Rasmussen *et al.*, 1976), 9, 74; Glasgow, IL (Rasmussen *et al.*, 1977), 5, 74; Rio Blanco Co., CO (Arnts and Meeks, 1981), 2, 74; Smoky Mountain National Park, TN (Arnts and Meeks, 1981), 2, 40; (Cronn and Harsch, 1980), 5, 40; and Florida sites (Lonneman *et al.*, 1978), 2–4, 30. Thus, even when the two compounds compared have almost equal atmospheric reaction rates (Arnts and Gay, 1979), the ratios computed from the ambient air measurements are much smaller than the ratios from emission inventory estimates. Similar high ambient air ratios also are obtained if acetylene is used rather than propene as a surrogate for anthropogenic HC emissions.

The ambient air ratios considered in the previous discussion were based on the average or median isoprene concentrations. It is possible that the higher isoprene concentrations may have a different relationship to the anthropogenic HCs at a rural site than do the average or median values for isoprene. Tabulated measurements of the ambient air concentrations of individual HCs are not available from many of the studies cited. However, at the Glasgow, IL site (Rasmussen, 1977), slightly over 200 analyses were obtained over a 26-day period. The 20 sampling periods with isoprene concentrations exceeding 10 ppbC were considered separately. 12 of these sampling periods occurred at night or near sunset. The isoprene concentrations in these 20 samples constituted from 10 to 23% and averaged 15% of the total non-methane HCs measured at the Glasgow, IL site. The range of isoprene to propene ratios varied from 9 to 54 with the average isoprene to propene ambient air ratio was 22. This ambient air ratio is higher than the ambient air ratios of 5 computed from the median concentrations, but still smaller than the corresponding emission ratio of 70. During a stagnation episode on one day (12 August 1975), the ratios varied from 18 to 54 and the highest ratios in the study occurred late in the afternoon and early in the evening hours of 44 and 54.

Concurrent ambient air measurements of α-pinene, acetylene and propene concentrations have been reported at several sites. To compare the ratios of ambient air concentrations of these HCs to the ratios from their emission inventories, the biogenic emission inventory for monoterpenes must be considered.

Although annual emissions for all monoterpenes from the contiguous United States has been estimated at 50 Mt (Zimmerman, 1979b), emission inventories were not provided for individual monoterpenes. However, the assumption that α-pinene constitutes about 1/2 of the total monoterpene inventory appears reasonable. The α-pinene was estimated as constituting slightly under 1/2 of the monoterpene inventory in the Tampa–St. Petersburg area (Zimmerman, 1979a). Based on this estimate and the annual U.S. propene emissions calculated earlier of 6×10^5 t y^{-1}, the annual average ratios of α-pinene to propene would be 42. The monthly average U.S. α-pinene emissions for January, July, August and September is estimated as 1.75×10^5, 5.5×10^6 and 4.3×10^6 and 3.1×10^6 t per month. Based on these estimated values and the previous assumption of equal emissions of acetylene and propene in each month of the year, the ratio of α-pinene to propene is as follows: January, 3; July, 92; August, 72 and September, 52.

The ratios of α-pinene to propene ambient air concentrations (Tables 7 and 8) compared to the emission inventory estimates made above are by site as follows: Elkton, MO (Rasmussen *et al.*, 1976), 0.6, 72; Glasgow, IL (Rasmussen *et al.*, 1977), 1, 72; Smoky Mountain National Pk, TN (Cronn and Harsch, 1980), 3, 52; Jones State Park, TX (Seila, 1981), 3, 3. The ratios of the ambient air concentrations are about a factor of 100 higher than the ratios of the emission inventories for the two midwest sites in the summer. The differences between these two sets of ratios are even larger than from the intercomparisons for isoprene to propene. The corresponding computations using acetylene rather than propene show similar results. The ratios at the Jones State Park site in January are the only ones in reasonable agreement. Similar ambient air ratios also are obtained if acetylene is used rather than propene as a surrogate for anthropogenic HC emissions. It is not clear why there should be such large differences on the average between the two sets of ratios.

It might be contended that none of the rural sites used were typical, but that they were unduly impacted

by local vehicular emissions on nearby rural roads. However, there is nothing in the descriptions available by the authors of the studies to confirm such an assumption. Almost any rural site selected in the eastern United States would be near light traffic from one rural road or another. These emissions are part of the over-the-road portion of the mobile source emission inventory. East of the Mississippi River only about 14,600 km^2 are considered mandatory Class I areas in National Parks, Wilderness Areas, and other unique areas (Council on Environmental Quality, 1978). Many parts of Class I areas may not be really remote. Even in the 1st and 2nd tier of states west of the Mississippi there are a few such areas which are of limited acreage. Only in portions of the far western United States are there large wilderness areas well removed from population centers which may be considered remote. However, ambient air measurements on the composition of HCs are not available for such areas which can be used for comparison.

There are a number of possible explanations for the poor agreement between the two sets of ratios. Several of these explanations might be concurrently applicable. These explanations are as follows: (1) The biogenic emission inventory is much too high. (2) The anthropogenic emission inventory is much too low. (3) The biogenic compounds react so rapidly in the atmosphere as to disappear before collection. (4) The biogenic compounds react rapidly with O_3 in the sampling container. (5) Most of the biogenic compounds are lost to the walls of the containers used during the storage period before analysis.

The fifth possibility listed above could apply to emission samples collected by the bag enclosure method. These samples are pumped into a stainless steel cannister and held in the cannister prior to analysis. Neither the fourth and fifth possibilities would apply to the measurements in several of the studies for which both the sampling and analysis was done at the rural site (Ferman, 1981; Rasmussen *et al.*, 1976, 1977; Stevens *et al.*, 1981).

The anthropogenic volatile organic compound emission inventories are based on diverse types of survey information, usage patterns, and engineering estimates. The vehicular emissions component has involved a substantial effort over a quarter of a century to measure the mass and composition of various vehicle types with changing emission control systems. Most of the results have been based on measurements of vehicles operated on dynamometers programmed to match certain driving cycles. The driving cycles have been developed from on the road vehicle operation over urban routes.

The limits of uncertainty of the various major components of the volatile organic compound emission inventory usually are not given. Independent verification through intercomparisons with air quality measurements are lacking. The emission inventories of interest here are those for non-urban areas which have received very little attention.

One effort to estimate HC emission inventories based on air quality model sensitivity testing was done for the Harris Co. (Houston) TX area (Ganesan, 1981). It was reported that increases of from 3- to 6-fold were needed in the reported HC emission inventory to obtain agreement with measured ambient air concentrations. The range, 3- to 6-fold, depended on the size of the box used in the model. A major HC emission inventory estimation problem in this area according to Mrinas and Trijonis (1979) is associated with fugitive emissions from petroleum refineries and chemical plants.

No seasonal adjustments were included in the calculation of anthropogenic emissions. However, temperature changes might be expected to affect emissions from mobile sources. While tailpipe emissions decrease with increasing temperature, (Ashby *et al.*, 1974; Braddock, 1981; Marshall and Eccleston, 1980) evaporative emissions increase with increasing temperature. Relationships have been developed relating losses to maximum daily temperature and Reid vapor pressure (RVP) for pre-1970 vehicles (Biller *et al.*, 1972). Evaporative emissions constituted 35–50% of total emissions (sum of tailpipe and evaporative emissions) with summer driving and fueling conditions (Black *et al.*, 1980). A study of the net effects of such temperature changes on emissions is available for older vehicles (Joint Project, 1969). Because of the compensating factors discussed above, the total emissions showed changes of $< 5\%$ with a change of 25 F in daily maximum temperature for four different fuel RVP's.

Based on the above results, seasonal temperature changes on vehicular emissions did not appear to be substantial so the relationship of a surrogate such as propene to total vehicular emissions should remain almost the same throughout the year.

The biogenic volatile organic emission inventories used to develop the U.S. and specific geographic area inventories are all based on the results from the bag enclosure technique. As already discussed, several intercomparisons have been made between the bag enclosure and micrometeorological technique procedures in forests. The agreement between the approaches is highly variable. Comparisons of predicted concentrations with observed concentrations have been made from the results of two micrometeorological field studies (Lamb *et al.*, 1981; Quarles *et al.*, 1980). In an oak forest measured and predicted concentrations of isoprene over the canopy showed differences varying from $+96$ to -19% (Quarles *et al.*, 1980). Similarly, in a forest predominately of Douglas fir measured and predicted concentrations of α-pinene just at the top of the canopy and above the canopy showed differences varying from $+74$ to -400% (Lamb *et al.*, 1981). A third technique involving measurement of downwind movement of a biogenic HC and a tracer, SF_6, with use of a multi-source Gaussian plume dispersion model has received preliminary evaluation recently (Arnts *et al.*, 1981).

Comparison of the fluxes of α-pinene from a loblolly pine forest by this diffusion model technique with previous results in another loblolly pine forest by a micrometeorological technique (energy balance/Bowen ratio technique) (Arnts *et al.*, 1978; Knoerr and Mowry, 1981) indicated that the micrometeorological technique yielded an emission rate six times higher than the diffusion model estimates. Another comparison (Arnts *et al.*, 1982) indicated fluxes computed by the bag enclosure procedure (Zimmerman, 1979b) were four times higher than the diffusion model estimates. Such comparisons between measurements at different sites and times probably are of limited applicability.

The above results suggest a substantial range of uncertainty in emission estimates of biogenic HCs from available techniques. Certainly, none of the techniques can presently be used as a reference method.

Measured ambient air concentrations can be compared with concentrations predicted from flux estimates for a particular forest area with certain meteorological conditions assumed. For example, Holdren and *et al.* (1979) treated the forest canopy as a box with a computed time to exchange its volume. The estimated total ambient concentration of 1.6 ppb (16 ppbC) was in good agreement with the highest measured concentration, but measured total monoterpene concentrations within the forested area varied from < 0.1 ppb to 1.6 ppb over a period of a week. The model was not used to account for such variations. Zimmerman (1979c) also used a simple box model to estimate the wind speed necessary to make the emission rate consistent with the ambient air concentration measured within 15–30 cm from branches. The computed wind speed was 0.76 m s^{-1} and the observed wind speed atop a field laboratory was 5.7 m s^{-1}. Zimmerman claimed that directionally lower wind speeds should occur near the ground within the canopy. In the same area away from the live oak trees no isoprene could be detected.

The third possible explanation of the large discrepancies between biogenic to anthropogenic ratios from emission estimates compared to measured ambient concentrations may involve the ambient lifetime of the HCs. If a HC reacted very rapidly from the source of emission to the sampling point, its concentration could decrease below its detectability limits. Within forest areas, the distances from the emitting trees to the sampling location usually would be in the range of 1–10 m. Samples taken within adjacent clearings should be within several hundred meters of the biogenic emission sources. Myrcene, a very rapidly reacting monoterpene even under middav summer environmental conditions, has a lifetime of 0.1 h (Table 10). At a windspeed of 10 km h^{-1}, myrcene would travel 1000 m downwind of its sources in a clearing before being consumed. Somewhat less reactive monoterpenes such as α-pinene under the same conditions would travel about 10 km downwind of its sources before being consumed.

As noted earlier, anthropogenic olefins such as *trans*-2-butene and 2-methyl-2-butene which have lifetimes of several tenths of an hour are detectable at rural sites. On the average, these olefins would be expected to travel substantially further from vehicular sources or gasoline storage facilities to the rural sampling locations than do the biogenic HCs from their sources.

Arnts *et al.* (1982) used a multi-source Gaussian plume dispersion model, PAL, to compute the concentrations of inert and chemically reactive species through a forest 10 km square. Two classes of atmospheric mixing were used at winds of 3.6 km h^{-1}, B stability, a high degree of mixing and E stability, a low degree of mixing. A steady state concentration of 0.05 ppm of O_3 and 3×10^{-8} ppm of OH radicals was assumed. The four chemical conversion rates selected corresponded to the following types of compounds: (a) an inert compound, (b) a compound with reactivity equal to α-pinene, (c) a compound slightly less reactive than D-limonene and (d) a compound with a reactivity about that of myrcene.

Under B stability, relative to an inert compound passing through 10 km of forest to the downwind edge of a forest, 84, 75 and 51% of compounds would remain with reactivities about equal to those of α-pinene, D-limonene and myrcene, respectively. Under E stability, relative to an inert compound passing through 10 km of forest to the downwind edge of a forest, 67, 52 and 25% of compounds would remain with reactivities about equal to α-pinene, D-limonene and myrcene, respectively. A larger forest would not affect these results because the compounds are already very near to steady state concentrations at or before 10 km distance.

Myrcene under the stability conditions given could first travel through the 10 km forest which was its source area and then ~0.5 km downwind before its initial concentration would be reduced to or below 10% of the concentration of an essentially inert compound. The concentration of α-pinene or isoprene would decrease by less than a factor of two relative to an inert compound under these same conditions.

Isoprene and propene react at nearly the same rate with O_3 so no change should occur in their ratios with such atmospheric reactions, while α-pinene would react only moderately faster than propene. Based on the discussion above, it is unlikely these small differences in chemical reaction rates in the atmosphere between emission and sampling accounts for any significant part of the discrepancies under consideration.

Another possibility is that when the HC is collected in a rigid container or bag, it will be consumed after collection, but before analysis by reaction with O_3. Since the anthropogenic olefins can be measured in samples collected in rural areas, the biogenic HCs if

they were present at the sampling location at the same or higher concentrations also should be measurable. In the studies in which smaller volume Tedlar bags were used, 10–20ℓ (Arnts and Meeks, 1981; Lonneman *et al.*, 1978; Seila, 1981) tests indicated that about 80% of the O_3 present in the ambient atmosphere was destroyed in the filling process and the remaining O_3 essentially gone after 30–60 min (Lonneman and Bufalini, 1979). If as much as 0.10 ppm of O_3 were originally present, 0.02 ppm would be available to react initially and 0.00 after 1 h. An average concentration of 0.01 ppm of ozone in one hour would not consume a substantial amount of isoprene, α-pinene, β-pinene, 3-carene or β-phellandrene. About 50% of the limonene or myrcene originally present might be consumed. In some studies, the collection containers were charged initially with NO to remove by chemical reaction the excess O_3 (Arnts *et al.*, 1978; Seila, 1981). In these studies, no subsequent olefin–O_3 reactions in the containers would occur. Therefore, this possibility also does not appear to offer an explanation for the large differences between emission and ambient air ratios of biogenic to anthropogenic HCs.

The last possibility to be discussed is that isoprene and monoterpenes might be lost in storage before analysis to a much greater extent than anthropogenic HCs. Holdren *et al.* (1979b) have measured the stability of a large number of HCs and oxygenated HCs in the stainless steel canisters used in some of the sampling discussed over a 3-week period. In this study, ambient air was used to dilute the HCs in order to simulate the effects of O_3 and other ambient species or HCs during storage. For the paraffinic and aromatic HCs evaluated the losses after 1, 2 and 3 weeks of storage were as follows: 1 week, +7 to −15%, 2 weeks, +5 to −28%, 3 weeks, −3 to −38%. For the four biogenic HCs evaluated the losses after 1, 2 and 3 weeks were as follows: isoprene, −4, −10, −17%; α-pinene, −9, −27, −60%; β-pinene, −16, −40, −73%; limonene, −27, −88, −100%. The losses for isoprene were in the same range as C_6–C_8 paraffins, but the losses for the monoterpenes after one week were substantially greater than those of the anthropogenic HCs tested. A loss of 17% for isoprene and 60% for α-pinene would not account for the discrepancy under consideration.

Lonneman and Bufalini (1979) reported on a 30-day storage study of monoterpenes in air in 2 mil Tedlar bags. The losses observed over a 30-day period were as follows: α-pinene, −3%; β-pinene, −9%; Δ^3-carene, −4%; D-limonene, −1%; myrcene, −2%. These losses are much too small to be of significance in explaining the discrepancies between emission and ambient air ratio of biogenic to anthropogenic HCs.

Of the various possibilities discussed above, the most likely ones to explain the larger part of the discrepancies are those associated with the emission inventories. The other possibilities appear capable at most of accounting for a small portion of the differences in ratios between source inventories and ambient air concentrations. A combination of an underestimate in the rural anthropogenic emission inventory along with a substantial overestimate in the biogenic emissions appears necessary to account for these differences in ratios.

8.2. *How completely have biogenic species been identified and quantitated?*

For oaks, isoprene is well established as the predominant biogenic compound emitted during the daylight hours. In the Tampa Bay emission survey (Zimmerman, 1979a), 10–20% of the emissions from oaks were reported as unidentified species, principally alkanes and other C_6–C_{12} volatile organic compounds (Table 1). At night when isoprene is not emitted, these unidentified species are assumed to remain. For pine, α-pinene and β-pinene are the most abundant species with D-limonene and Δ^3-carene reported as emitted in substantial amounts from several pine species (Table 1). The monoterpene, Δ^3-carene, also was reported as an important product in emissions of red cedar and cypress, while D-limonene has been reported as an important product in the emissions from tomatoes (Zimmerman, 1979a). Other monoterpenes and oxygenated products such as myrcene, phellandrene, camphene, tricyclene, *p*-cymene, terpinolene and methyl chavicol are occasionally detected as minor emission products (Flyckt, 1979; Tingey *et al.*, 1979; Westberg, 1981; Zimmerman, 1979a). For the number of types of vegetation, only a minor number of emission products have been identified (Zimmerman, 1979a, b). These include the southern red cedar, red maple, wax myrtle, red bay, mangroves, Carolina ash, American elm and some other trees and scrubs, orange and grapefruit trees, strawberries, grasses and field crops, such as corn (Zimmerman, 1979a, b). These latter species have been reported to emit small amounts of many compounds complicating the problem of identification (Flyckt *et al.*, 1980). Grasses and corn are examples. Because such species cover large acreages, better identification of their emission products would be desirable. Without such measurements it is difficult for areas covered by field crops and pasture to adequately estimate biogenic emissions. The emission products from sclerophyll scrub species also are not identified (Zimmerman, 1979b).

8.3. *How effective are biogenic HCs in contributing to the formation of O_3 in the atmosphere and how does this potential compare with that of anthropogenic HCs? What are the amounts of biogenic HCs available in the ambient air to generate O_3?*

To consider this issue laboratory studies must be used to estimate the O_3-forming potential of individual compounds and mixtures of compounds and these results must be combined with appropriate ambient air measurements at rural sites to predict ozone formation.

In the earlier discussion of O_3 formation in Section 7, the potential for ozone formation in terms of ratios of O_3 produced to volatile organic compound consumed was discussed. The behavior of the multi-component mixtures with respect to O_3-forming potential, compared to the behavior of the single HC systems with increasing HC to NO_x ratio, suggest a substantial narrowing of O_3-forming potentials for HC mixtures of complex compositionunder ambient air field conditions (Table 12). No more than a 2:1 range appears likely to apply to O_3-forming potentials of complex multi-component atmospheric mixtures. The O_3 production per 100 ppbC of HC mixture based on the experiments considered above appears to be in the range of 10–30 ppb of O_3.

If the 10–30ppb of O_3 per 100ppbC of HC is accepted as a useful, although perhaps conservative estimate, the range of HC concentrations at rural sites in the United States of 50–200 ppbC (Section 7) could produce from 5 to 60 ppb of O_3. This is the potential for O_3 production of the ambient air mixture measured at rural sites downwind of these sites.

In Table 15 are summarized the percentage of average total non-methane HCs present as isoprene and monoterpenes at various rural sites. The isoprene and monoterpenes made up from 1 to 9% of the average HC content measured at the sites in the United States and ranged from 1 to 7 ppbC. These amounts of isoprene and monoterpenes based on the average O_3-production of 0.1 of these compounds could form 0.1 to 0.7 ppb O_3.

HC and O_3 measurements along with meteorological data are available from the study at the Glasgow, IL site (Rasmussen *et al.*, 1977). During 8, 9 and 10 August, 1975 the air arriving at the Glasgow, IL site appears to have originated from St. Louis (Rasmussen *et al.*, 1977). The evidence for this includes the elevation of CCl_3F as a tracer of urban activities, wind speed and direction measurements at Glasgow, and wind speed and direction measurements downwind in the RAPS network in St. Louis (Shreffler and Evans, 1982). The O_3 inflow concentration during these 3 days from 1200 to 1500 CST at Glasgow was higher than average, but were still lower than the O_3 inflows into St. Louis (Shreffler and Evans, 1982). The maximum 1-h O_3 concentrations on 8, 9 and 10 August at Glasgow, IL of 130, 92 and 95 ppb were among the highest O_3 concentrations measured at the site (Rasmussen *et al.*, 1977). These peaks occurred at 1600, 2000 and 1700 hrs CST 3 to 5 h later than the peaks in the St. Louis area. The highest O_3 concentrations on these dates within the RAPS network occurred on each of the 3 days at site 121 (Shreffler and Evans, 1982). The maximum 1-h O_3 concentrations at Glasgow were 10, 74 and 42 ppb less than at site 121. During the hours when O_3 attained its maximum concentrations, non-methane HC concentrations reached 140 ppbC, 150 ppbC and 100 ppbC on 8, 9 and 10 August 1975. During these same hours, the isoprene and α-pinene concentrations summed to 6, 5 and 11 ppbC. Only a small portion of the O_3-producing potential of the HCs in the plume after its passage over rural terrain could be associated with these two biogenic HCs at these concentration levels.

On 12 August, 1975 the meteorological conditions were of such a nature as to lead to a stagnation situation in the region around Glasgow, IL (Rasmussen *et al.*, 1977). This area was on the northwest side of a high pressure system centered in the SW United States. The O_3 concentration exceeded 80 ppb at 1000 h CST and remained above 80 ppb until it peaked at 1900 h CST at slightly over 100 ppb and

Table 15. Contribution of isoprene and monoterpenes to total nonmethane hydrocarbon concentrations

		Average/median concentration (in ppb C)		
Authors	Geographical location	Isoprene and monoterpenes	Total non-methane hydrocarbon (NMHC)	Percentage of NMHC as isoprene and monoterpenes
Rasmussen, *et al.* (1976)	Elkton, MO	7	80	9
Rasmussen *et al.* (1977)	Glasgow, IL	4	100	4
Lonneman *et al.* (1978)	Florida			
	orange grove	4	112	4
	Tampa Bay area	1	53	2
	everglades	1	94	1
Zimmerman (1979)	Houston, TX area			
	near live oak	4	133	3
	near slash pine	2.5	45	5
	near common fig	6	400	2
	near red bay	7	150	5
Seila (1981)	Jones State Forest, TX			
	picnic area	3	122	3
	forest canopy	3	170	2
Arnts and Meeks (1981)	Rio Blanco Co., CO	2	124	2
	Great Smoky Mt. TN	4	110	4

then dropped off rapidly. The non-methane HC concentration was about 160 ppbC at the time the O_3 peaked at 1900 hours CST and continued to increase to above 200 ppbC at 2200 h CST. If the HC concentration in the plume during the hours before the air reached Glasgow was about the same as measured at Glasgow and an O_3-producing potential of 30 ppb of ozone per 100 ppbC is assumed, the O_3 production would be in the range of 40–50 ppb. If a 50 ppb clean air background (Kelly *et al.*, 1982; Singh *et al.*, 1978) is added, the observed O_3 concentration can be accounted for satisfactorily.

The isoprene concentrations during the daylight hours on 12 August 1975 at Glasgow varied from 6 ppbC up to 30 ppbC and constituted from 5 to 20% of the non-methane HC at Glasgow (Rasmussen *et al.*, 1977). Based on the same O_3-production potentials as assumed above, the concentrations of O_3 associated with these concentrations of isoprene would be 2–10 ppb of O_3. The α-pinene concentrations measured were too low to make a substantial contribution to the O_3 formed based on the assumptions above. The O_3 estimated to be formed from the biogenic HCs is a small portion of the total O_3 observed.

Ganesan (1981) considered the natural HC emissions as well as the anthropogenic emissions of HCs and NO_x in model calculations of O_3 formation in the Houston plume. Based on the emission inventories, an 18% contribution of natural HCs to the total HC emission rate was obtained. However, the model prediction was that only 2.4% of the ambient air HCs were from vegetation. The maximum O_3 concentrations predicted increased by 8 ppb from 232 to 240 ppb if it was assumed that only natural HCs were added to the plume from forested areas as the Houston plume traveled downwind. In a second scenario, it was assumed that additional NO_x emissions, presumably of anthropogenic origin, would be added to the plume at 10% of the rate in the urban area. This assumption resulted in the maximum O_3 concentration increasing by 11 ppb from 232 to 243 ppb. These incremental O_3 concentrations of 8 and 11 ppb were only a few per cent of O_3 measured in the plume.

8.4. *What is the potential of biogenic HCs compared to anthropogenic HCs to participate in the formation of aerosols in ambient air?*

The potential of various HCs including biogenic HCs to participate in the formation of aerosols was discussed in Section 7. The results considered in Section 7 were those obtained from laboratory studies. It will be assumed that these experimental results can be extrapolated to the atmosphere. In order to discuss the contributions to atmospheric aerosol formation of the various groups of volatile organic compounds which are moderate to strong aerosol producers, it also is essential to know the atmospheric concentration levels of these compounds. Atmospheric measurements are available, but not complete for some classes of aerosol-forming compounds, and unavailable for other classes of compounds. When atmospheric measurements are not available, source measurements can be used to estimate the relative amounts of the various groups of aerosol-forming compounds emitted to the atmosphere. Gasoline is the source of most of the groups of HCs of higher molecular weight which have aerosol-forming potential. The HC groups of particular interest are the aromatics, C7 and higher molecular weight acyclic olefins and the cyclic olefins.

Gas chromatographic analyses by carbon number in the C_1–C_{12} range are available for paraffins, olefins, and aromatics from twenty gasolines obtained in five eastern cities in the summer of 1980 (Midwest Research Institute, 1980). The content in % and ratios of the aromatic HCs and the C_7 and higher olefins are given in Table 16. The ratios obtained indicate that the concentrations of aromatics should be in large excess to C_7 and higher olefins in the atmosphere.

Additional results are available from the detailed gas chromatographic analyses and subtractive techniques by Sanders and Maynard (1968) on regular and premium grade gasolines. The ratio of aromatics to C_7 and higher olefins in the regular grade gasoline was 35:1 and for the premium grade fuel 46:1. Sanders and Maynard also separated and measured the cyclic olefins. The ratio of aromatics to cyclic olefins in the regular grade fuel was 130:1 and in the premium grade fuel was 48:1.

Dimitriades *et al.* (1972) obtained gas chromatographic analyses over a wide molecular weight range on vehicle exhausts from three gasolines. The ratios of aromatics to C_7 and higher olefins and of aromatics to cyclic olefins for the three fuels were as follows: fuel 1, 12 and 35; fuel 2, 18 and 55; fuel 3, 65 and 82.

The ratios of aromatics to the two olefin subclasses of interest as aerosol precursors were large in all three studies (Dimitriades *et al.*, 1972; Midwest Research Institute, 1980; Sanders and Maynard, 1968). Based on single HC studies on the aerosol-forming ability of

Table 16. Ratios of the organic aerosol precursors—aromatic hydrocarbon to seven carbon and higher olefins in gasolines

Type	Number of gasolines	Average aromatic content, %	Average, C_{7+} olefin content %	Ratios	
				Average	Range
Leaded regular	7	30.46	1.14	27	15 to 392
Unlead regular	8	38.64	1.05	37	20 to 4840
Unleaded premium	5	46.10	0.93	50	31 to 140
All gasolines	20	37.7	1.05	36	

aromatics and these ratios of concentrations, aromatic HCs would be expected to predominate over fuel olefins as aerosol formers in the ambient atmosphere.

Measurements are not available on the very small concentration levels of individual C_7 and higher acyclic olefins or on cyclic olefins which may be present in urban or rural atmospheres. Measurements are available for aromatic HCs. Therefore, the only direct comparisons of concentrations possible are between anthropogenic aromatic HCs and the monoterpenes. Comparison of average aromatic HC to α-pinene concentrations at the same rural sites indicate the following ratios: Elkton, MO (Rasmussen *et al.*, 1976), 8; Florida sites (Lonneman *et al.*, 1978), > 100; Jones State Forest, Texas (Seila, 1981), picnic area, 5 and forest interior, 11: Glasgow, IL (Rasmussen, 1977), 4; Great Smoky Mountain National Park (Arnts and Meeks, 1981), 20. In the analyses at the Elkton, MO site from 1/3 to 2/3 of the aromatic HCs were unidentified when compared to gasoline, automobile exhaust analyses, and ambient urban air analyses. Therefore, the ratios at these sites probably should be multiplied by factors of 1.3–1.7. At other rural locations the underestimates of aromatics were smaller. Conversely, it is conceivable that traces of some other of the monoterpenes may have been missed. However, in several of the investigations at rural sites the concentration levels of several other monoterpenes is reported to be below detectability limits of about 0.1 ppbC.

Alpha-pinene which is the terpene most frequently identified has an organic aerosol-forming potential which appears to be a factor of 5–10 higher than aromatic HCs (Grosjean, 1977). Therefore, even though aromatic HCs may exceed monoterpenes in concentration by a substantial factor in rural areas, their relative contributions to aerosol formation may be within a factor of 2 of each other in rural areas.

The aerosol study by Miller and Joseph (1976) for mixtures containing aromatic HCs as the predominant aerosol precursors has been discussed in Section 7. The aerosol volume, computed in $\mu g\,m^{-3}$ per ppbC of aromatic increases with decreasing aromatic concentration. At the lowest concentration of aromatic HCs, this parameter averages about $0.02\,\mu g\,m^{-3}$ of aerosol per ppbC of aromatic HCs.

In the Smoky Mountains, where 20 ppbC of aromatics was observed by Arnts and Meeks (1981), use of a factor of $0.02\,\mu g\,m^{-3}$ of aerosol formed per ppbC of HC consumed leads to a prediction that about $0.4\,\mu g\,m^{-3}$ of organic aerosol could be present from reaction involving aromatic HCs. The natural aerosol would be generated from the estimated α-pinene concentration of 1 ppbC (Arnts and Meeks, 1981). If α-pinene is 5 to 10 times more effective in producing aerosol (Grosjean, 1977) and the concentration of α-pinene is 1/20 that of the aromatics, the aerosol yield should be in the range of 1/4 to 1/2 of that produced from the aromatics or $0.1–0.2\,\mu g\,m^{-3}$. Therefore, the potential estimated total organic aerosol concentration which could produce from these measured aerosol precursors at the Smoky Mountain site would be predicted as in the range of $0.5–0.6\,\mu g\,m^{-3}$. Cronn and Harsch (1980) reported an α-pinene concentration of 4 ppbC. The same type of calculation leads to an aerosol yield of 0.4 to $0.8\,\mu g\,m^{-3}$ and an estimated total organic aerosol concentration from precursors of $0.8–1.2\,\mu g\,m^{-3}$.

Another approach to estimating the aerosol from the α-pinene involves use of the results of studies reported by Kamens (1981) and Hull (1981). Kamens (1981) reported that at least 25% of the C from α-pinene ozonolysis could be in the form of aerosols. While Hull (1981) found at high precursor concentrations almost all of the products from ozonolysis of α-pinene were in the condensed state, he indicated that much of this condensed material would be vapor at ambient air concentration. In particular, Hull (1981) obtained a yield of 27% for *cis*-pinonic acid from the reactions of α-pinene. This product which was identified earlier by Schwartz (1974) is the least volatile of the products identified and the most likely compound to be found in the atmosphere as an aerosol. Therefore, 1 ppbC or $0.56\,\mu g\,m^{-3}$ of α-pinene at the Smoky Mountain site would produce about $0.15\,\mu g\,m^{-3}$ of *cis*-pinonic acid and 4 ppbC would produce $0.6\,\mu g\,m^{-3}$. These results are in good agreement with the previous estimates. The other monoterpene studied by Hull (1981), β-pinene, did not form *cis*-pinonic acid or other products with vapor pressures as low as *cis*-pinonic acid. Therefore, even if a trace of β-pinene was present, it would appear not to be as effective aerosol producer as α-pinene. Isoprene does not appear to be effective in production of visibility-reducing aerosols (Kamens *et al.*, 1981).

In comparison with these estimates of aerosol concentrations, Stevens *et al.* (1980) measured a mean fine particle organic aerosol concentration of $2.2\,\mu g\,m^{-3}$ at the same site in the same time period. These investigators found that the dominant fine aerosol was acid sulfate with a mean concentration of $13.5\,\mu g\,m^{-3}$ which exceeded organic aerosol in concentration by a ratio of 6:1. Stevens *et al.* (1982) also made aerosol measurements in the Shenandoah Valley of Virginia in 1980. The mean fine particle organic aerosol at this site was $0.9\,\mu g\,m^{-3}$. In the form of NH_4HSO_4, the mean concentration of sulfate aerosol was $16.0\,\mu g\,m^{-3}$ exceeding the organic aerosol in concentration by a ratio of 18:1. It appears likely that most of the sulfate would have been transported into the area and would have formed from sulfur oxide emitted from anthropogenic sources well upwind (Stevens *et al.*, 1980a). Therefore, part of the organic aerosol content could have been transported into the area also.

The highest average concentrations of α-pinene usually are observed within forest canopies have reached 10 to 20 ppbC. Using the conversion factor of $0.15\,\mu g\,m^{-3}$ per 1 ppbC of α-pinene, these α-pinene concentration levels might produce a maximum of 1.5

to 3 $\mu g\,m^{-3}$ of organic aerosol as *cis*-pinonic acid under stagnant conditions with limited local dilution within forest canopies.

In the eastern United States, these concentration levels of aerosols estimated as forming from monoterpenes do not appear likely to constitute a substantial fraction of the total fine particle aerosol concentrations measured at urban or rural sites.

9. CONCLUSIONS

(1) The ambient air concentrations measured of isoprene and monoterpenes are very low (Tables 7 and 15). Except within forest canopies the total concentrations of these biogenic HCs usually range between 1 and 10 ppbC. Within forest canopies the higher concentrations usually range between 10 and 100 ppbC. However, other measurements within forest canopies indicate concentrations below 10 ppbC. Some scattered measurements above 100 ppbC have been reported during periods of leaf drop and near isoprene sources during a hot summer day. Isoprene usually is the most abundant biogenic HC measured except within monoterpene-emitting forests.

(2) The concentrations of biogenic HCs usually constitute less than 10 percent of total HCs measured at a number of rural sites (Table 15). Occasionally, the biogenic HCs measured have constituted somewhat higher percentages of total HCs such as during stagnation conditions.

(3) Substantial differences in predicted fluxes are obtained for biogenic HCs by the various techniques available. The comparisons made are limited by the extrapolations necessary between different locations, times, and variations in species.

(4) The ratios of biogenic HCs such as isoprene or α-pinene to propene obtained from ambient air measurements is almost always much lower than the ratios calculated from emission inventory results. The explanation for this discrepancy does not appear to be atmospheric disappearance of biogenic HCs before measurement, or losses in collection, storage or analysis. This leaves as possibilities overestimations of the biogenic emission inventory combined with underestimations of the non-urban anthropogenic emissions inventory.

(5) Although several oxygenated HCs have been measured in emissions from a few biogenic sources, no ambient measurements are available indicating these oxygenated HCs to be significant in concentration. However, relatively little work has been done to collect and analyze for such oxygenated HCs.

(6) The contribution of the biogenic HCs measured at rural sites to O_3 formation does not appear from available estimates to be significant under most atmospheric conditions.

(7) The available measurements in the eastern United States lead to estimates that organic aerosols formed from biogenic HCs do not contribute a significant fraction of the total fine particle aerosol concentrations at urban or rural sites.

(8) Biogenic HC concentrations within urban areas will tend to be lower than in rural areas because of less dense emission sources, while anthropogenic HCs are at higher concentration within urban areas because of denser emission sources. Therefore, the contribution of biogenic HCs to O_3 and aerosol formation within urban areas will be less than in rural areas.

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